AN INVESTIGATION INTO THE BEHAVIOUR OF COBALT IN THE SOIL.

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I declare that the work described here is my own and that the thesis was composed by myself.

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THESIS ABSTRACT

The extraction of cobalt from 3 soils with 0.5 M acetic acid was studied under conditions of varying temperature, duration of extraction and soil-solution ratio. The first two parameters significantly affected the quantity of cobalt extracted, but variation in soil-solution ratio had little effect.

In an examination of 20 soils from south-east Scotland, the total soil cobalt content was found to be positively correlated with the concentrations of iron and manganese oxides. Extractability studies using 0.5 M acetic acid and 0.04 M di-sodium EDTA indicated that cobalt was associated to a greater degree with the manganese oxides than the iron oxides. However, the 0.01 M $CaCl_2$-extractable cobalt concentration was not related to the soil oxide content, but was negatively correlated with soil pH. Isotopic exchange studies showed that the concentration of isotopically exchangeable cobalt was directly related to the soil oxide content. The equilibrium between isotopically exchangeable cobalt on the solid phase of the soil and in soil solution was highly dependent on soil pH.

No relationship between total, extractable or isotopically exchangeable cobalt and soil organic matter was observed.

In an incubation study waterlogging caused mobilisation of both indigenous and added cobalt, as determined by acetic acid extraction. Drying of the soil to 20 per cent moisture caused rapid immobilisation of this cobalt and, over a period of months, the supplementary cobalt became non-extractable.

The specific sorption of cobalt by individual soil constituents and by 18 soils from south-east Scotland was examined. The equilibrium solution cobalt concentrations used were those likely to be found in soil (10^{-6} M). Amorphous soil oxide material showed the highest capacity for sorption, followed by humic and fulvic acids and then montmorillonite. However, the reaction between cobalt and montmorillonite showed greater irreversibility than with humic acid. The sorption characteristics of the intact soils indicated that sorption took place predominantly on the manganese oxide fraction.

Two pot experiments were carried out to study the uptake of native cobalt by perennial ryegrass and red clover and also the increase in the cobalt content of perennial ryegrass following application to the soil. The concentration of plant cobalt derived from indigenous soil supplies was negatively correlated with soil pH, as was the increase in plant content due to artificial addition to the soil. The latter quantity was also negatively correlated with the soil iron and manganese oxide contents.

Field trials were set up in south-east Scotland to monitor the effect of top-dressing with cobalt on uptake by deficient pasture (mixed herbage). Over a 3 year period, the addition of 6 kg $CoSO_4.7H_2O$ per hectare raised herbage cobalt concentrations to above 0.08 µg/g (deficiency level) in less than half of the 15 soils studied. Applying the same amount of cobalt as the EDTA complex was still less effective. Although herbage cobalt concentrations decreased over the 3 year sampling period, there was no concurrent decrease in acetic acid-extractable soil cobalt. Most of the applied cobalt was present in the top 4 cm of soil.

CONTENTS

INTRODUCTION

Cobalt is one of a large number of elements found in trace quantities in plants and animals. At the present time, only a small proportion of these elements have been found to be essential for plant growth, namely:- iron, manganese, copper, zinc, boron, molybdenum and chlorine. Although cobalt has not been found to be essential for plant nutrition, yield increases resulting from cobalt application to leguminous plant species have been obtained (Ozanne et al. 1962; Wilson and Hallsworth,. 1965). It appears that cobalt has an essential role in nitrogen fixation by rhizobium bacteria in the root nodules of leguminous plants (Reisenauer, 1960). There have also been reports of yield increases in cereal crops as a result of cobalt application to soil (Young, 1979).

Animals require the trace elements named above, except for boron and, in addition, animals also require iodine and selenium.

Cobalt is required in animals as a part of the vitamin B_{12} complex (cyanocobalamin). In non-ruminants the vitamin B_{12} complex is acquired pre-formed in the diet. In ruminants it is synthesised by micro-organisms in the rumen, from dietary cobalt. The animal subsequently absorbs the vitamin B_{12} into the bloodstream.

Where there are low levels of dietary cobalt in the ruminant, vitamin B_{12} deficiency symptoms are observed. It is generally thought that levels of cobalt below 0.08µg/g of feedstuff dry matter are deficient for sheep nutrition. The deficiency level may be slightly higher for cattle. The symptoms of deficiency are loss of appetite and body weight, loss of coat condition and anaemia. This can be

attributed to the depressed activities of the two vitamin B_{12} - containing enzymes in the animal (Smith and Gawthorne, 1975).

Sub-clinical cobalt deficiency can also be observed in livestock where, although the concentration of cobalt in the diet is above the deficient level, it is below that required for optimum live weight gain.

Although the wasting condition in livestock had been reported for many years previously, it was not until the 1930s that the symptoms were attributed to low cobalt levels in pasture. In South Australia, sheep grazing on calcareous sands of the coastal littoral showed a condition known as 'coast disease' which was alleviated by the oral administering of cobalt to the sheep (Marston et al. 1938, reported in Lee, H.J., 1975). In Western Australia, a similar condition known as 'Denmark wasting disease' in sheep and cattle was also alleviated by the administration of cobalt (Underwood and Filmer, 1935, reported in Lee H.J., 1975). Bush sickness in New Zealand was also attributed to a cobalt deficient diet (Grange and Taylor, 1932), and top-dressing of pastures with cobalt salts was carried out in order to alleviate the condition (Askew and Dixon, 1937; Dixon and Kidson, 1940). In the Cheviot Hills of Scotland, Corner and Smith (1938) treated unthriftiness in sheep, known as 'pine' by the oral administration of cobalt. In the 1940s in Scotland, experiments were conducted in the Solway and Easter Ross regions to overcome pine in sheep by top-dressing pasture with cobaltous chloride and dosing lambs with cobalt (Stewart, Mitchell and Stewart, 1941, 1942; Stewart, Mitchell, Stewart and Young, 1946).

Cobalt deficiency in Scotland is commonly found in the Solway area, the Border region, north-east Scotland and in coastal regions of north-west Scotland and the Outer Hebrides. Areas particularly affected are those where the soils are formed from Old Red Sandstone, granites, calcareous sands and where peat soils, formerly used only for rough grazing, have been reclaimed in order to support a more intensive grazing system.

The diagnosis of deficiency of cobalt in soils, with respect to plant availability, has commonly been by the use of acetic acid (0.5M or 2.5% solution) as a soil extractant. Its ability to give a good indication of plant available soil cobalt levels has been questioned, however.

Diagnosis of cobalt deficiency in livestock is normally carried out by measuring cobalt levels in the blood serum or, in a dead animal, cobalt levels in the liver.

At present a common means of alleviating cobalt deficiency in livestock is to top-dress pasture with cobalt salts. The rate of application usually used in Scotland is 2.0 to 2.5 kg $CoSO_4.7H_2O$ per hectare, which is intended to increase cobalt levels in deficient herbage to above 0.1µg/g D.M. for at least 3 years. In the soils of the Border region the rate of application is 6 kg $CoSO_4.7H_2O$ per hectare to one-quarter or one-third of the field area. This ensures that herbage cobalt levels are sufficient in part of the field. McLaren et al. (1979) showed, however, that the response of herbage cobalt levels at sites in the Border region to this high rate of cobalt application were variable. At one site the herbage cobalt concentration was below that required for healthy ruminant nutrition only one year after top-dressing of the pasture.

Other methods of preventing and alleviating cobalt deficiency include the provision of salt licks containing cobalt and the supplementing of concentrate rations with a cobalt mineral. Although expensive and time consuming, livestock may be drenched with cobalt salts or alternatively, cobalt oxide 'bullets' can be administered, which slowly release cobalt into the reticulum.

It was one of the aims of the present study to monitor the uptake of cobalt by pasture herbage, over a number of years, from soils top-dressed with cobalt sulphate. These soils were in areas of the Border region of Scotland where cobalt deficiency in sheep has been reported. One purpose of this investigation was to explain the variability in herbage cobalt levels in response to the top-dressing of pasture with cobalt, as observed by McLaren et al. (1979).

Another objective of the study was to investigate the properties and constituents of soils which are likely to be of importance in controlling the plant-availability of both native and applied cobalt. It was also intended to study the ability of 0.5M acetic acid soil cobalt extraction to reflect the quantity of plant-available cobalt in soil.

CHAPTER 1. LITERATURE REVIEW

1.1 Distribution of Cobalt in the soil

1.1.1 GEOLOGICAL OCCURRENCE OF COBALT

The cobalt content of a soil depends primarily on the geological material from which it was formed. This is particularly evident where the soils are young and have undergone little weathering.

In the formation of igneous rocks, the ultrabasic magmas crystallise out first, followed by the basic and finally by the acidic rocks. Cobalt, along with the trace metals nickel and chromium, is preferentially incorporated into the more basic rocks. This class of material includes the ferromagnesian minerals, such as olivines and pyroxenes, which incorporate Mg^{2+} and Fe^{2+} in a silicate lattice structure. Any other cation of a similar ionic radius to these ions present in the crystallising magma (eg Co^{2+}) can equally well occupy such sites in the lattice. Thus cobalt is progressively depleted in the magmas during the process of crystallisation and rocks crystallising at a later stage, such as rhyolites and granites, tend to have lower concentrations of trace metals such as cobalt (Mitchell, 1964).

The process of soil formation involves the weathering of these igneous rocks either directly to soil, or indirectly through the formation of sedimentary rocks. The rate of chemical weathering of the igneous rock depends on its mineral constituents. The bulk of the biologically important trace elements, such as Zn, Mn, Co and Cu, occurs in the more

easily weathered constituents eg olivine, hornblende and biotite (Mitchell, 1964).

In the process of rock formation by sedimentation, the silicates reorganise to form hydrolysed alumino silicates with a layer lattice type structure. Trace metals such as cobalt either remain with, or become associated with, these secondary minerals by surface adsorption and isomorphous substitution (Hodgson, 1963). These minerals will go through further morphological changes during soil formation, but cobalt will remain associated with them. Before isomorphous substitution occurs in the clay mineral the metal is probably held at surface octahedral sites, in which case the ionic radius and charge on the ion are important in preferential adsorption. Andersson (1977), working with soils in Sweden, noted that as the ionic radius of trace metals with co-ordination number 6 decreased the correlation between concentration of a specific trace metal and the clay content of the soil increased. This emphasises the importance of the ionic radius of the trace metal for incorporation into the clay mineral.

Sandstones are comprised almost entirely of minerals which weather with difficulty and would be expected to produce soils which are deficient in available trace elements (Mitchell, 1964).

Mitchell (1964) measured the trace element content of the surface layers of 9 Scottish arable soils derived from different geological parent materials. The total cobalt concentration ranged from below 3 ppm, in the sandstone and

granitic soils, to 80 ppm in a soil derived from serpentine. In deficient acid soils the total cobalt contents are generally in the range of < 0.5 ppm to 3 ppm. Contents of up to 50 ppm are common in soils carrying healthy livestock. Swaine (1955) and Vinogradov (1959) both reported 8 ppm cobalt as a typical concentration in soils.

1.1.2 FORMS OF COBALT IN SOIL

Along with other trace metals, such as copper, zinc and nickel, cobalt is present in a number of fractions of the soil. A large proportion may be associated with unweathered primary minerals in the soil, either as constituents of the crystal lattice or by sorption of soil cobalt into these minerals. A proportion of the soil cobalt will be associated with the clay minerals either by simple ion exchange or more probably by specific adsorption. This is the sorption of a metal cation on a solid surface with greater energy than that from simple ion exchange at negative sites. The ion is thus preferentially held on the surface in the presence of high concentrations of competing ions in soil solution. The phenomenon of specific adsorption is particularly common with metal ions in the first transition series of the periodic table.

Another fraction of soil cobalt may be associated with the oxides of iron, manganese or aluminium through co-precipitation, occlusion or bound at the surface by specific adsorption.

Soil organic matter also plays a role in the sorption of soil cobalt although the strong relationship found between copper and soil organic matter is not so evident with cobalt.

There is incorporation of cobalt into the bodies of micro-organisms in the soil. This would probably be in the form of the vitamin B_{12} complex.

Finally, a very small proportion of cobalt will be present in the soil solution.

Association of Cobalt with the soil clay fraction

The association of cobalt, along with other trace metals such as zinc, with the clay fraction of soils has been demonstrated from the results of a number of investigations.

Hill et al. (1953) noted, in two New Jersey Coastal Plain soils, that cobalt concentration increased with decreasing particle size and that, within each particle size range, the cobalt content tended to increase with depth from the A_1 to the C horizon.

An analysis of surface soils from Finland showed, in general, a difference of 4 to 5 times in total cobalt content in ranging from sandy soils to heavy clays (Vuorinen, 1958).

Again, in Finland, Silanpää and Lakanen (1966) obtained an inverse relationship between ammonium acetate - soluble cobalt and the coarseness of texture in topsoil samples of mineral soils. Enrichment in the clay fraction was also exhibited by Andersson (1979) in samples of the lower part of B horizons of the 5 different Swedish soils. However, cobalt was enriched in the clay fraction to a lesser extent

than zinc, copper, nickel or chromium.

The association of cobalt with the soil clay fraction has been established at many centres. In soils of the New England states of the USA, Kubota (1964) found cobalt concentration to increase fivefold from the sand to the clay fraction. In Nova Scotia there was a high negative correlation between the concentration of cobalt and the percentage of sand in soil (Wright and Lawton, 1954) and in Quebec Province, Canada, Rana and Ouellette (1967) observed that the total cobalt content of a particular soil was directly correlated with, and greatly dependent on its clay content.

The same phenomenon has been observed in Finland (Silanpää, 1962a), Sweden (Andersson, 1977), Pakistan (Wahhab and Bhatti, 1958), Gujarat State in India (Reddy and Mehta, 1961) and in some soils derived from quartz dolerite in Tasmania (Tiller, 1963).

Areas of cobalt deficiency in which livestock have received inadequate supplies of cobalt have been found on predominantly sandy soils in New Hampshire, USA (Lyford et al., 1945) and in Jutland, Denmark (Nielsen, 1969).

Swaine and Mitchell (1960), however, in studying 8 soil profiles in Scotland, noted little variation between horizons in total contents of trace metals. Although there was a decrease in the extractable cobalt content from surface to the C horizon, in a freely drained cultivated podzol, it occurred irrespective of a change in clay content between the horizons.

Association of Cobalt with soil amorphous oxides

Cobalt is known to be associated with the amorphous oxide fraction of the soil either by surface adsorption or by occlusion during the formation of the oxide. A relatively large amount of work has been carried out which demonstrates the association of cobalt with iron and manganese oxides.

Le Riche and Weir (1963) extracted the iron oxides from two brown earth soils using ammonium oxalate under ultra violet light. The concentrations of iron in the extracts were almost the same for the surface and B horizons of both soils, but cobalt, along with copper, manganese and lead was more concentrated in the surface soil extracts. Overall the enrichment factor of the oxalate extract was so great that, although only 5% by weight of the soil was dissolved, it contained over half the total content of these elements. However, it must be noted that the oxalate also dissolved organic matter and that, on the evidence of the high concentrations of manganese in the oxalate extracts, manganese oxides were also dissolved.

Soil cobalt levels have been shown to parallel the distribution of sesquioxides in Grey-Brown and Brown Podzolic soils (Wright et al. 1955) and to follow the distribution of iron in podzolised soils (Kubota and Lazar, 1960).

Kubota (1965) observed that in the surface horizons of podzols and ground-water podzols of the eastern USA there were only small amounts of total and dithionite-extractable

cobalt. The latter quantity was assumed to be from the iron oxide fraction of the soils. However, those surface horizons with a textural B layer contained appreciably more total and dithionite-extractable cobalt. This suggested that the amorphous oxides were associated with the clay fraction, possibly by the formation of coatings, and these were responsible for adsorption of cobalt. It is probable that the results of many workers, showing the relationship of cobalt with the clay fraction, were caused by adsorption of cobalt into oxide surface coatings.

From the upper horizons of six morphologically different soils Rerikh et al. (1975) extracted the free oxides of iron, aluminium and manganese using Tamm's acid oxalate and noted that in the krasnozems there was a high cobalt content in the extract, reaching 48% of the total content. There was little readily reduced or total manganese in the krasnozems but there was a large amount of non-silicate iron. This would imply that the iron oxides were of importance in the sorption of cobalt. However, this result does not preclude the possibility of the manganese oxides being relatively more important than the iron oxides in cobalt sorption.

In podzolic soils of Tasmania, there was an accumulation of cobalt reported in ironstone concretions (Tiller, 1963). However, Swaine and Mitchell (1960) found no evidence for an accumulation of 2.5% acetic acid - extractable cobalt in the iron pan of podzols in some Scottish soils.

Direct association of cobalt with manganese oxides has been demonstrated by Taylor and McKenzie (1966) and Taylor (1968) and a partial association of cobalt with manganese down a krasnozen profile was reported by Tiller (1963) working on soils, in Tasmania, derived from dolerite.

Poole et al. (1974), on investigating a case of cobalt deficiency in lambs in the North Leinster region of Eire noticed that although soil tests indicated levels of cobalt not normally deemed as deficient, the pasture herbage was deficient in cobalt. They suggested that cobalt was being immobilised in the soil, possibly by manganese oxides, since these soils had high total manganese levels of 1,000 to 1,750 ppm.

Association of Cobalt with soil organic matter

The remarkable affinity for copper shown by soil organic matter is not so marked for cobalt. This may be accounted for in terms of the strength of complexes formed between the reactive functional groups of the organic matter, such as carboxyls, and the metal ions (Schnitzer and Skinner, 1967).

However, the fact that cobalt does enter into organic complex formation is important in that it prevents cobalt from entering into exchange and sorption reactions with the mineral fraction of the soil. Consequently the distribution of cobalt within the soil may be strongly influenced by the soil organic matter in the short term, although eventually cobalt will be released by mineralisation of the organic matter. A number of workers have reported a poor correlation between soil cobalt and organic matter. (Wright and Lawton, 1954;

Andersson, 1977; Rana and Ouellette, 1967; Silanpää, 1962a). In contrast, McLean and Langille (1976), studying soils in Nova Scotia, demonstrated that cobalt extractable by 0.1N HCl did increase with soil organic matter content.

Peat soils are likely to be low in cobalt as a result of dissociation of the surface soil from the parent geological material and its weathering products. If the surface peat layer is deep the vegetation does not have access to cobalt in the subsoil, and thus no cycling of the element takes place. In the eastern counties of Eire, Finch and Rogers (1978) noted many cases of cobalt deficient peat soils, particularly in cut-over and improved raised bogs.

Hodgson et al. (1965) studied low molecular weight organic complexes of cobalt, copper and zinc, using displaced soil solutions. They demonstrated that the proportion of complexed cobalt present in the soil solution was low, as compared with copper and zinc. It is likely then, that cobalt organic complexes are less important than those of copper and zinc for the movement of these elements within soil profiles.

Kubota (1965), however, suggested that chelated forms of cobalt may be important in its downward movement in podzols. In podzolic soils of the eastern USA he observed that cobalt was displaced further down the profile than iron. He suggested that this may have been due to the greater stability of soluble cobalt-organic matter complexes than those of iron.

More general studies on podzolised soils have shown them to be relatively low in cobalt (Rana and Ouellette, 1967; Kubota, 1964). Apart from the effects on cobalt content from leaching in podzols, a low innate cobalt content would be expected as a result of the coarse, sandy nature of these soils.

1.2 Factors affecting plant uptake of Cobalt

The availability of soil trace metals for uptake by plant roots is dependent on the forms in which they are present in the soil. For instance, trace metals present in the primary minerals, derived from physical breakdown of the parent geological material, will not be available to plant roots. Only after weathering of these minerals will any constituent trace metals be released to take part in reactions with other soil constituents or to be absorbed by the plant.

Hodgson (1963) illustrated the reactions in which trace metal cations are likely to participate. These included formation of soluble and insoluble organic complexes, surface adsorption, diffusion into soil minerals, occlusion within developing precipitates in the soil, precipitation of the metal oxide and incorporation into microbial tissue.

The plant root is probably only able to absorb cobalt which is adsorbed on surfaces and which is in soil solution. It may also have the ability to absorb cobalt in soluble organic complexes in the soil solution, but, as was mentioned previously, the concentration of these is likely to be small.

The chemistry of the sorption reactions and organic complex formation of cobalt with soils and soil material is considered more fully in section 1.5.

Of the soil properties which affect plant uptake of cobalt the two most important are known to be soil pH and the drainage status of the soil. The uptake of cobalt will also be affected by the species of plant and its stage of maturity.

1.2.1 SOIL pH

The plant availability of cobalt, along with other trace metals such as zinc, has been shown by a number of workers to be pH dependent. (Reith and Mitchell, 1964; Beeson et al. 1948; Singh and Singh, 1966; Graham, 1973).

In a comparison of the cobalt content of pasture and soils from 8 sites in Yugoslavia, Mokragnatz and Filipovic (1961) reported that there was no direct correlation between the cobalt content of the herbage and that of the soil. However, cobalt content was a function of soil pH, the content decreasing with increasing pH.

Coppenet et al. (1972), in Britanny, measured the uptake of cobalt by Italian rye grass on soils derived from granitic rock. Liming of the soil caused a dimunition of plant cobalt, whereas the addition of ammonium nitrate caused an increase as a result of soil acidification. In pot trials the authors noted a dimunition in plant cobalt of up to 20% for an increase in soil pH of 0.7 to 0.8 units.

On studying the uptake of soil cobalt by subterranean clover Nicholls and Honeysett (1964b) noted that soil pH was one of the factors governing the ability of plants to absorb applied cobalt. However, on measuring the uptake of native cobalt by subterranean clover, the authors did not detect any trend of plant cobalt content with soil pH (Nicholls and Honeysett, 1964a).

1.2.2 SOIL DRAINAGE STATUS

The association of cobalt with soil oxides was mentioned previously, and it is evident that the proportion and form of these oxides in the soil will play an important role in the amount of cobalt withdrawn from solution. The form of the oxides is greatly influenced by the redox potential of the soil, which in turn is affected by the moisture status of the soil. This will also affect the forms of organic matter in the soil, and consequently the solubility of any organo-cobalt complexes formed.

Measurements of available soil cobalt using 0.5M acetic acid have shown it to extract over twice the amount of cobalt from a poorly drained soil as from a well drained soil in the same area (Mitchell et al., 1957).

Adams and Honeysett (1964) grew subterranean clover on 4 different soils in glasshouse conditions and measured the effect of soil waterlogging on the plant uptake of trace elements. With 9 days of soil waterlogging during the growth of the clover, the copper, nickel, iron, zinc and manganese concentrations increased by 2, 7, 10, 22 and 60% respectively. These values compared with a 91% increase in cobalt concentration. Proportions of these concentration increases were caused by the stunted growth of the plants in the waterlogged conditions.

By increasing the temperature during waterlogging of the soil before sowing of the clover, the differences in cobalt concentration between plants on non-waterlogged and waterlogged soils became greater. The increase in cobalt concentration

was also affected by the stage of plant growth at which the soil was waterlogged, the effect being greater at the later stages of growth.

When waterlogging conditions were severe the plants were much reduced in size and showed symptoms of manganese toxicity. It is probable that the enhanced cobalt uptake was, to a large extent, a consequence of the reduction of manganese oxides in the soil under the prevailing reducing conditions. This would cause the release of sorbed and occluded cobalt into solution. The authors also observed that waterlogging had much less effect on the copper content of the plants than cobalt. Copper is not thought to be so strongly associated with the soil oxide fraction as cobalt.

The general observation was also made by the authors, that the krasnozems of Tasmania, although rich in total soil cobalt, often carry cobalt deficient livestock. These soils are never waterlogged. The meadow-podzolic soils are waterlogged every winter and, although low in total cobalt content, they are not known to carry cobalt deficient livestock.

1.2.3 STAGE OF PLANT MATURITY

Askew and Maunsell (1937) reported cobalt concentration in forage to be high in spring with a decrease during the growing season. The phenomenon was also reported by Fleming and Murphy (1968) who noted a decline in cobalt concentration in perennial ryegrass with advancing maturity. However, Beeson and McDonald (1951) noted an increase in the

concentration of cobalt in timothy grass as it matured and Mitchell et al. (1957) also noted an increase in the cobalt content of mixed herbage during the growing season.

1.2.4 COMPOSITION OF PASTURE SWARD

It has been reported by a number of authors that leguminous species contain greater concentrations of cobalt when grown in the same soil as grass species.

Andrews (1966) in New Zealand, showed that when cobalt was sufficient in the soil, legumes accumulated more than grasses. However, differences were negligible on cobalt deficient soils. Beeson and McDonald (1951) reported a lower concentration of cobalt in timothy than in ladino clover or birdsfoot trefoil.

A requirement by subterranean clover for cobalt was noted by Ozanne et al. (1962) and yield increases of 30% were obtained in response to dressings of up to 625 g $CoSO_4.7H_2O$ per hectare. Clover growth was sharply reduced when the cobalt concentration fell below 0.04 ppm in the herbage. This effect was also reported by Wilson and Hallsworth (1965). Gladstones et al. (1977) studied the responses to cobalt application by 6 different legume species and noted an enhancement of root nodule growth. This stimulated greater cytokinin production which caused an increase in leaf growth.

1.3 The Assessment of Plant Available Cobalt in the Soil

1.3.1 EXTRACTABLE SOIL COBALT

The concentrations of plant available trace metals in the soil are very small in comparison to those of other metal ions such as sodium, potassium and calcium. In the case of cobalt it is mainly the small fractions present in the soil solution and on the exchange sites which are available. Difficulties arise in the use of an extracting solution which displaces only these forms of soil cobalt, since analysis of the resulting solutions would be beyond the capability of routine analytical methods.

The extractants commonly used to assess the plant availability of soil cobalt have, almost certainly, been displacing fractions of soil cobalt which are not exploited by the plant root.

The extractant used most commonly to assess soil deficiency in plant available cobalt has been acetic acid, either a 2.5% or 0.5 M solution.

It is generally held that soils containing less than 0.25 ppm acetic acid - extractable cobalt will carry cobalt deficient herbage (< 0.08 ppm Co in dry matter) (Mitchell, 1963).

Mitchell et al. (1957) studying soils of north-east Scotland demonstrated that there was a highly significant correlation coefficient between the concentration of soil cobalt extracted by 2.5% acetic acid and the cobalt contents of the associated pasture herbage. However, by taking 0.25 ppm acetic acid-extractable cobalt as the borderline between a

sufficient and deficient soil, the results showed that a fairly large proportion of the sites had cobalt deficient herbage on soils deemed to contain adequate available cobalt.

Mitchell (1945) had previously reported the diagnosis of cobalt deficiency by 2.5% acetic acid to be unsatisfactory in soils previously top-dressed with cobalt and in shell sands containing free $CaCO_3$.

Conducting a pot experiment by growing Sorghum vulgare on 21 representative soils of the Gujarat region in India, Reddy and Mehta (1961) found 2.5% acetic acid to exhibit a better correlation with plant uptake than 0.1 N HCl, ammonium acetate at pH 4.5 and neutral 1 N ammonium acetate.

In Kentucky, USA, Seay and de Mumbrum (1958) measured the amount of cobalt in lespedeza against that extracted from soil by a sequential 0.5 M acetic acid extraction. However, no significant relationship was obtained between the 'available' soil concentration of cobalt and that in the plant.

In an investigation into the effect of soil moisture conditions on the uptake of cobalt by alsike clover, Kubota et al. (1963) demonstrated that, for the dryer soil treatment, there was an increase in plant cobalt content with an increase in total, acetic acid-extractable and soil solution cobalt. However, only 4 soils were used in this study.

To acquire information on the soil components from which acetic acid extracts cobalt, Rana and Ouellette (1967), in

Quebec, Canada, measured the concentrations of 2.5% acetic acid-extractable cobalt in samples from 30 soil series. The extractable cobalt was significantly correlated with total cobalt and soil clay content in surface soils. However, overall, the variables studied (ie total cobalt, per cent clay, organic matter, pH) did not explain the variability observed in the extractable content of different soils. The soil extraction period was one hour instead of the more common 16 hour period.

Kubota (1965) found acetic acid-extractable cobalt to increase with dithionite-extractable cobalt in soils from the south-east of the USA. This result, and others mentioned previously, indicates that the cobalt being extracted by acetic acid is strongly sorbed to soil oxides.

Ammonium acetate, at either acid or neutral pH, has also been investigated as a suitable extractant for soil cobalt. In Finland, Silanpää and Lakanen (1969) reported acid ammonium acetate (pH 4.65) to be suitable for the determination of plant available cobalt. Analysis of over 400 topsoil samples using acid ammonium acetate gave average cobalt contents similar to those obtained by Mitchell (1964) in Scotland using acetic acid (Silanpää and Lakanen, 1966).

Banerjée et al. (1953) concluded that cobalt added to soil could be extracted in two forms. That which remained easily exchangeable was soluble in neutral ammonium acetate whereas the strongly adsorbed fraction was obtained by leaching with 0.1 N HCl. Similar results were obtained by Rerikh et al.

(1976) using cobalt-60 as a radioactive tracer for added cobalt and extracting with ammonium acetate at pH 4.8.

In Australia, Tiller et al. (1969) attempted to identify the forms of cobalt contributing to isotopically exchangeable cobalt in 25 soils using 1 N ammonium acetate at pH 7.0, followed by hydroquinone to extract the fraction sorbed by manganese minerals. The sum of the amounts extracted was significantly correlated with 20 of the soils. There was no correlation for the 5 prairie soils studied. These had relatively high total cobalt, ammonium acetate exchangeable and hydroquinone - reducible cobalt contents, and they also contained a high percentage of montmorillonitic clay.

Gille and Graham (1971), conducting experiments on the uptake of trace metals by sudangrass from a Mexican silt loam proposed 0.1 N HCl soil extraction to give a good estimation of the 'quantity' of cobalt in the soil, that is the total exchangeable cobalt in the soil. They also proposed 0.1 M $CaCl_2$ to give the best indication of the 'intensity' of cobalt in the soil. This is the fraction present in soil solution. It was suggested by the authors, that an effective extracting agent should show differences in the 'intensity' in solution rather than differences in the total amount of exchangeable cobalt in the soil.

In Nova Scotia, McLean and Langille (1976) noted that 0.1 N HCl extracted 10 to 20 per cent of the total cobalt in the soil. The extractable cobalt did not appear to be related to soil pH. However, extractability did increase with organic

matter and clay content of the soil.

Since acidic extracting reagents dissolve a part of the mineral constitutents of soil, thus releasing non-plant available cobalt, chelating agents such as ethylene diamine tetra acetic acid (EDTA) have been used in the assessment of available cobalt in the soil. These complex cobalt in soil solution and on the exchange sites. However, EDTA may also dissolve non-crystalline iron and manganese oxides in the soil to some extent; and it will also extract a large proportion of the soil organic matter.

Mitchell et al. (1957), using 50 soils from north-east Scotland, demonstrated a highly significant correlation coefficient for soil cobalt extracted by 0.05 M EDTA (pH 7.0) against herbage growing on these soils. In plotting herbage cobalt content against the extractability of soil cobalt, there was a smaller scatter of points with EDTA extraction than with acetic acid extraction.

Soils with impeded drainage, leading to an accumulation of organic matter in the surface horizon, may exhibit 0.05 M EDTA - extractable cobalt levels 2 to 3 times that of 2.5% acetic acid, whereas in normal agricultural soils, EDTA extracts slightly less cobalt than acetic acid (Mitchell, 1972). This emphasises the ability of EDTA to extract cobalt from the organic fraction of the soil, although there is uncertainty as to whether this fraction is important in supplying plant-available cobalt.

In New Zealand, Forbes (1976) extracted cobalt from samples of yellow-brown pumice soils using a 0.02 M EDTA/ 0.1 M NH_4Cl mixture at pH 5.5. This extracted amounts of cobalt similar to those extracted by acidified hydrogen peroxide. Thus the organically bound cobalt was being extracted by the EDTA solution, although the H_3O^+/H_2O_2 treatment also released a large amount of soil manganese from the soil oxides. It is also likely the EDTA was releasing cobalt from this fraction.

Lopez and Graham (1972) used a 0.005 M DTPA/0.1 M sodium acetate/0.01 M $CaCl_2$ mixture to estimate the labile pool of cobalt in soils, measured by isotopic exchange methods. The results showed that the DTPA (diethylene triamine penta acetic acid) mixture removed a major proportion of the labile pool and the authors suggested that the mixture could be used to estimate the labile pool of cobalt in soils suffering from severe deficiency. The labile pool is that quantity of the element present in the solid and solution phases of the soil which is able to exchange with cobalt in the alternate phase.

In Finland, Lakanen and Ervio (1971) conducted a pot experiment using oats grown on 3 soils: a fine sand, sphagnum peat and a sample of gytjja clay subsoil. Incremental amounts of trace metals were added to the soils before sowing. Eight extraction techniques were used on the soils after harvest of the oats. In all cases plant uptake of cobalt showed a significant correlation with soil

extractable cobalt. Acid ammonium acetate/0.02 M EDTA and neutral ammonium acetate/0.02 M EDTA were the two most powerful extractants for cobalt followed by 0.02 M EDTA at pH 4.6. Neutral 1N ammonium acetate extracted the least amount. From the results the authors suggested that acid ammonium acetate/EDTA would be a suitable extractant for trace metals along with soil macronutrients such as potassium. It is doubtful, however, that the ability of an extractant to displace cobalt previously added to the soil, as in this experiment, will give an indication of its ability to assess the quantity of native plant available cobalt in the soil.

1.3.2 ISOTOPIC EXCHANGEABILITY OF SOIL COBALT

Isotopic exchangeability of soil cobalt has been previously mentioned with reference to chemical soil extractants and comparisons have been made between these measurements in soil (Tiller et al. 1969). Isotopic exchangeability is a means of measuring the exchangeability of an ionic species on the solid phase of a soil with that fraction of the same ion in the solution phase. Tiller et al. (1969) applied the methods of isotope exchange developed for soil phosphorus to the study of exchangeable cobalt in soils. Two methods were investigated. In the first, chemical equilibrium was achieved in the system before an aliquot of the radioisotope cobalt-60 was added and allowed to partition itself between the solid and solution phases. In the second method, non-radioactive cobalt was applied to the system along with cobalt-60 and chemical and isotopic equilibria were achieved simultaneously. The values for isotopically exchangeable

cobalt obtained by the latter method were only slightly higher than those from the former.

The analysis was conducted on 25 soils and, in general, it was found that the soils with the largest proportion of cobalt which was isotopically exchangeable had the lowest cobalt contents. For 20 of the soils, the isotopically exchangeable cobalt contents were significantly correlated with the sum of the amounts of cobalt extracted by ammonium acetate and quinol, which were assumed to extract solution and easily exchangeable cobalt, along with that sorbed on manganese oxides. The authors concluded that the amount of isotopically exchangeable cobalt in a soil may provide a useful measure of the capacity factor of cobalt availability to plants.

Lopez and Graham (1972) investigated the equilibrium concentrations of the trace elements in soil solution and solid phase using isotopic exchange. A number of solution media were used in the measurements. The authors defined the isotopically exchangeable fraction as the 'labile pool' of soil trace elements. Its method of determination was similar to that of Tiller et al. (1969) and the most suitable solution medium was found to be a DPTA, $CaCl_2$, sodium acetate mixture. The labile pool measurement for cobalt was affected by solution pH and was generally higher at pH 5 than at 6, 7 or 8. In the soils studied the labile pool values ranged from 0 to 2.04 ppm Co.

A comparison between the plant uptake of cobalt and isotopically exchangeable cobalt in soil was made by Gille

and Graham (1971) using sudangrass. The calculation of isotopic exchangeability was similar to those of Larsen (1952) and Fried and Dean (1952). The effects of soil pH and the addition of Fe, Al and Ca to the soil on the plant uptake of trace elements and their isotopic exchangeability were also studied. There was an increased assimilation of cobalt by the sudangrass when Fe, Al and Ca were added to the soil and this was considered to be caused by a change in the 'intensity' of cobalt in the soil. However, no statistically significant differences were found in the values for the isotopically exchangeable cobalt in the soil attributable to change in soil pH or treatment.

Using radioisotopes, Graham (1973) measured the selective distribution coefficients of trace metals against standard amounts of solution calcium. The author suggested that labile pool measurements were of little significance, in themselves, for plant availability studies and would be of greater value if used along with the distribution coefficient. In soils where the labile pool for a given trace metal was high it could be anticipated that distribution of the element, between solid and solution phases, would control the concentration of the nutrient in plant tissue. The author maintained that plotting the selective distribution against labile pools of soil trace metals appeared to be a useful method for studying the trace metal status of soils regardless of their pH, clay or organic matter content and suggested that the information obtained would correlate with crop uptake for most common crops. However, as pointed out by the author,

the suggestion was based on the results from only 9 soils from a wide geographical distribution.

1.4 Application of Cobalt to soil

Soil application of cobalt is used as a means to increase the cobalt content of deficient pastures to a level greater than 0.08μg Co/g dry matter. Some of the first topdressing experiments were carried out by Askew and Dixon (1937) in New Zealand and in Scotland by Stewart et al. (1941, 1942, 1946). In the latter experiments a top dressing of 2 kg $CoCl_2$ per hectare was found to prevent and cure pining in lambs on the cobalt deficient areas of Easter Ross.

Rossiter et al. (1948) in Australia applied 0.25 and 0.5 kg $CoSO_4.7H_2O$ per hectare and measured the cobalt uptake by subterranean clover at 3 stages of growth. Three months after the application the higher rate of cobalt had produced a cobalt concentration in the clover of 0.41 ppm. After 15 months, however, this had fallen to 0.15 ppm. These values compare with 0.05 ppm Co in herbage without application.

In New Hampshire, USA, Percival et al. (1955) observed that an application of cobalt sulphate at the rate of 5 kg per hectare would supply forage crops with adequate cobalt, with respect to ruminant nutrition, for up to 5 years.

An application of 1.5 kg $CoSO_4.7H_2O$ per hectare to a deficient soil in Aberdeenshire caused a tenfold increase in the cobalt concentration of the pasture (Mitchell et al. 1957).

Reith and Mitchell (1964) applied cobalt to 2 typically deficient soils in the field and measured its uptake by a number of herbage species at various times of sampling. The authors suggested, from the uptake by mixed herbage, that a dressing of 2 kg $CoSO_4.7H_2O$ per hectare should maintain adequate herbage cobalt levels on a slightly acid cobalt-deficient soil. However,

on a calcareous soil, the effect of cobalt application was smaller, and it was concluded that a 4 kg per hectare application was required for such soils to maintain herbage levels above 0.08 ppm over a 3 year period.

Cobalt was also applied as the EDTA compound and, except for the period immediately after application, there was less uptake of this form than the sulphate salt. This was apparent even on calcareous soils on which the cobalt - EDTA complex would have been expected to provide a greater amount of plant available cobalt than the sulphate.

McLaren and Williams (1981) conducted a pot experiment to measure the uptake of soil applied cobalt and copper by perennial ryegrass and red clover from a mineral-deficient soil. Cobalt sulphate was applied to the soil at a rate equivalent to a field dressing of 6 kg per hectare. Two harvest cuts of the herbage were taken and at both cuts the treatment produced large increases in the cobalt content of ryegrass and clover. The equivalent addition of cobalt as the EDTA complex produced similar large increases in both species at the first cut, but only in clover at the second.

In contrast, cobalt applied to the soil as the EDTA complex was taken up by Ph vulgaris to a greater extent than from the cobalt sulphate application. The soil used was a calcareous loam (Wallace and Mueller, 1973).

Adams et al. (1969) applied approximately 1 kg $CoSO_4.7H_2O$ per hectare to a number of soils in Tasmania and the pasture uptake of cobalt was measured. In general, the response was greatest in the humus podzols, and least in the prairie and krasnozem soils. By measuring cobalt uptake by subterranean clover from the same soils

in pots, these authors demonstrated that there was poor agreement between the results of the pot and field experiments. It was suggested that the poor correlation was caused by the sensitivity of soil cobalt availability to physical conditions in the soil. As noted previously, in Section 1.2 soil drainage conditions have a major effect on the availability of soil cobalt.

From the results of both experiments, it was apparent that the humus podzols were the only soils in which cobalt application was effective for 2 years or more, whereas on the other soils, the effects of the application lasted only about one year. In general, the residual effect of the application was directly related to its effectiveness in the first harvest of clover.

The uptake of soil applied cobalt by subterranean clover, perennial ryegrass and white clover was measured by Nicholls and Honeysett (1964b) using 27 soils from Tasmania, Victoria and New South Wales, Australia. Cobalt was applied, in solution, to the surface of the soils in pots at the equivalent rates of 1.1, 2.0, 2.25 kg of $CoSO_4.7H_2O$ per hectare. In half of the soils, addition of the cobalt failed to increase the cobalt content of the plants. The data obtained strongly suggested that soil pH was one of the factors governing the ability of plants to assimilate applied cobalt, and it appeared that this cobalt was almost completely fixed in the soil when the soil pH exceeded 5.7. It has also been found, by Beeson et al. (1948), that the uptake of applied cobalt by soybeans is reduced by the application of limestone to the soil.

Relatively little research has been undertaken into the most suitable cobalt compound for soil application. As previously stated,

comparisons have been made on plant uptake between soils dressed with $CoSO_4$ and Co EDTA (McLaren and Williams, 1981; Reith and Mitchell, 1964; Wallace and Mueller, 1973).

Young (1955) investigated the solubility of various cobalt salts in a sandy clay loam soil in columns percolated with rain water over a period of 9 months. In the early period of the experiment, cobalt added as the nitrate salt was much more soluble, in the soil, than the chloride or sulphate. However, the powdered metal, carbonate, oxide and phosphate were all very slowly soluble. Only very small fractions of the latter additions were rendered soluble after a period of 9 months. By subsequently leaching the soil columns with 0.1N HCl the small remaining amounts of the chloride, nitrate and sulphate salts were eluted. Large proportions of the remaining elemental cobalt and phosphate applications were solubilised but very little cobalt was removed from the oxide and carbonate treatments by the HCl.

In pot trials, Coppenet et al. (1972) assessed the most efficient method of cobalt application to soil for plant uptake. The largest enrichment of cobalt in grass was with a dry top-dressing of already planted ryegrass as compared to incorporation into the soil or leaf spraying with a 0.001% solution of $CoSO_4$.

1.4.1 THE TRANSLOCATION AND DISTRIBUTION OF APPLIED COBALT

The downward movement of cobalt applied to soil was investigated by Jones et al. (1957). Radioactive cobalt-60 was applied to the tops of soil columns and its downward movement traced using a Geiger-Muller tube, with the successive additions of percolating solutions containing firstly inactive cobalt followed by zinc, copper, a

superphosphate suspension, a water extract of lucerne and finally CO_2 saturated water. Only in the two light, sandy soils was there any leaching of the cobalt-60. To one of the remaining soils, which had a high cation exchange capacity, a solution of EDTA was added and this caused 63 per cent of the radioactive cobalt to be eluted from the column, the remainder staying at the surface. It would appear probable that in this experiment, the EDTA extracted cobalt which was sorbed on the amorphous oxide fraction along with a certain amount associated with the organic matter. The fraction which remained at the top of the column was probably bound firmly to the organic matter by chelation. Forbes (1976) working with yellow-brown pumice soils concluded that cobalt, added as fertiliser, accumulated in the top 7.5 cm of soil.

The soil constituents with which added cobalt becomes associated has been the subject of a study for a number of authors. Zende (1954) added 40 ppm of cobalt to 4 different soils and left them exposed to the weather for 4 months. They were then extracted with 1 M ammonium acetate and 0.5 M $Ca(NO_3)_2$, with or without 0.2% quinol. Soils to which lime had previously been added, with a resultant higher pH, reduced the level of extractable cobalt. The 2 soils in which there was a prevalence of sand liberated more cobalt than the clay soils. When quinol was present in the $Ca(NO_3)_2$ extracting solution, there was an increase in the quantity of cobalt extracted. This may have been Co^{3+} in the soil

reduced to Co^{2+} or Co^{2+} strongly adsorbed on soil minerals. The soils were then sequentially extracted with EDTA until practically no further cobalt was extracted. A further extraction, using 0.2% quinol, caused a sharp increase in the amount of cobalt solubilised and the author postulated that this increment was the cobalt present in the soil as Co^{3+}. However, the quinol was probably of more importance in reducing soil manganese oxides, thus liberating associated cobalt.

Similarly Banerjée et al. (1953), using cobalt-60 radioisotope as a tracer, showed that cobalt added to the soil became present in 2 forms. These were easily exchangeable, as extractable by neutral 1 N ammonium acetate and strongly adsorbed cobalt, extractable by 0.1 N HCl. This strongly sorbed fraction was not present immediately after cobalt application, but its concentration increased with time. The authors suggested that there may also have been precipitation of added cobalt, especially in the presence of free anions.

Again, using the radioisotope cobalt-60 as a tracer; Rerikh et al. (1975) incubated soils, with additions of cobalt, for 2 years and using soil extractants, attempted to discover in which soil fractions the isotope was present as compared to the distribution of native cobalt.
In all the soils studied there was a decrease over time in the ammonium acetate - extractable cobalt-60, the largest decrease being in soils with the highest pH. A relatively large amount of the native, non-active, cobalt was bound to the argillic minerals although no cobalt-60 was detected

there. The amount of cobalt-60 bound to the amorphous iron, aluminium and manganese oxides was small, although it increased with time. The concentration of the native cobalt in these oxides was high however. The authors suggested that the most strongly bound cobalt was fixed in the organic matter, possibly as Co^{3+} complexes.

1.4.2 COBALT APPLICATION TO SOIL CONSTITUENTS AND ITS SUBSEQUENT PLANT AVAILABILITY

Comparisons have been made in the ability of different soil constituents to supply cobalt to plants from quantities of the metal ion previously applied to these constituents. Graham and Killion (1962) measured the uptake of radioactive cobalt-60 by rye, garden peas and soybeans from cobalt-60 impregnated soil materials. For rye, the highest cobalt uptake was from illite, followed by kaolinite, Putnam clay, fibrous peat, sedimentary peat and finally montmorillonite.

The plant uptake of cobalt from soil minerals was also measured by Kabata and Beeson (1961). Varying amounts of cobalt were applied to the minerals followed by a wash with 0.1 N $CaCl_2$ to desorb electrostatically bound cobalt. Ladino clover and orchard grass were grown on the materials and the resultant plant uptake of cobalt was found to be greatest from muscovite, followed by haematite and finally bentonite and kaolin. However, the amount of cobalt soluble in 0.1 N HCl was greatest in bentonite and least in kaolin and haematite. The only correlation between the amount of acid-soluble cobalt in the substrate and cobalt in the plants was with bentonite. The authors

concluded that there were obvious differences in the mechanism of cobalt sorption by the minerals.

1.5 Sorption of Solution Cobalt by Soils and Soil Materials

Characterisation of the sorption behaviour of soil solid constituents towards solution cobalt may have practical implications in assessing the capacity of a soil to immobilise fertiliser cobalt or to allow it to remain plant available. Sorption experiments on soils and individual soil components in different solution conditions have also been used in attempts to elucidate the type of bonds formed between cobalt and the solid phase of the soil. Because of the small quantities of cobalt present in soils it is clear that normal cation exchange reactions will not be of importance in holding cobalt on the solid phase because of the large quantities of ions, such as calcium, competing for these sites. Consequently cobalt is held at more selective sites by processes known collectively as 'specific adsorption'.

1.5.1 SORPTION ON INTACT SOILS

Forbes (1976) sorbed solution cobalt and copper onto samples of the yellow-brown pumice soils of New Zealand and noted that cobalt sorption increased markedly over the solution pH range 3.5 to 5.5, although copper was extensively sorbed at all pH values in this range. At pH values greater than 6.0, the sorption of both cobalt and copper decreased with increasing pH and this was probably caused by the dispersion of organic matter into solution, carrying complexed metal ions with it.

This effect of pH was also observed by Prokhorov et al. (1979) in the USSR. The sorption maximum for cobalt was at pH 7.5 to 8.5 in the 5 soils studied. The authors concluded that below this pH range there was competition

for exchange sites from H^+ ions in solution. At pH values greater than 8.5 they suggested that calcium ions were competing for exchange sites and that there was partial dissolution of the soil organic matter.

The above two studies emphasise the role of soil organic matter in the sorption of cobalt, although Prokhorov et al. placed greater importance on the competitive behaviour of calcium in the high pH systems than on the desorption of organo-metallic complexes into solution.

Tiller et al. (1969) measured the adsorption of cobalt by 25 soils and produced adsorption isotherms for specifically adsorbed cobalt. These were calculated by subtracting the concentration of cobalt bound at the 'normal' cation exchange sites from the total concentration adsorbed. The saturation capacity and bonding energy of the soils were calculated from the Langmuir equation. There was a highly significant correlation obtained between the Langmuir sorption capacity term and the manganese content of the soils. The bonding energy gave a consistent value in soils of varying mineralogical composition and organic matter content. The authors assumed that there was one dominant surface for cobalt sorption in these soils and that this was a manganese oxide surface.

Using the same 25 soils as above, Adams et al. (1969) compared the uptake of applied cobalt by clover with the initial slope of the sorption isotherms obtained by Tiller et al. (1969); that is the portion of the isotherms which referred to low surface coverage of cobalt on the soils.

The recovery of applied cobalt by clover was negatively related to the initial slope of the adsorption isotherm. Thus the greater the soil's ability to specifically adsorb cobalt the less cobalt was extracted by subterranean clover.

Working with soils of varying mineral composition, Abd-Elfattah and Wada (1981) sorbed various trace metals onto them and concluded that there was a parallel between the selective sorption of metal ionic species and its ability to hydrolyse or form a hydroxide precipitate. From the extent of specific sorption on the various soils the mineral constituents which appeared to be of importance were in the order:- iron oxide > halloysite > humus, allophane-imigolite, kaolinite > montmorillonite, allophane.

Since sorption studies with intact soils only provide information by implication concerning the soil components which are important in cobalt sorption, experiments have been conducted on individual soil components to assess their sorption capacity for cobalt.

1.5.2 SORPTION ON CLAY MINERALS

Much effort has been spent on studying the reactions of cobalt with clay minerals derived from soil or of geological origin. Results have led to a certain amount of speculation as to the mode of sorption involved.

Andersson (1977), in Sweden, measured the sorption of cobalt as a function of pH on kaolinite, montmorillonite, amorphous iron oxide, an illitic subsoil and two organic soils. Kaolinite and iron oxide proved to be poorer adsorbents

for cobalt at acid pH than the illitic subsoil which, in turn, was poorer than the organic soils. Montmorillonite was as effective an adsorbent as the organic soils.

A comparison was made in the sorption activity between geological clay minerals and clay minerals extracted from soil by Tiller et al. (1963). There were considerable differences found in the amount of cobalt specifically sorbed by a range of pure minerals at varying solution pH. However, when cobalt was sorbed on the same minerals extracted from subsoil, there was little variation in the amount sorbed. The reactions took place at the low cobalt concentrations likely to be encountered in soil solution, with a background concentration of 0.1 N $CaCl_2$ to avoid non-specific cobalt adsorption on the clays. Treatment of the soil-derived clays to remove any residual organic matter and amorphous oxide coatings, resulted in a very slight enhancement of sorption in some soil clays with the removal of oxide material. This is surprising, in that the amorphous oxide coatings are thought to play a relatively large role in cobalt sorption and their removal would have been expected to decrease cobalt sorption.

In an attempt to explain the difference in behaviour of the soil and geological minerals, the authors proposed that, in comparison to the relatively stable environment of the geological material, soil clay minerals suffer from physical abrasion and chemical weathering and that the resultant structural defects may be the major sites of cobalt adsorption.

Thus any effect structural differences between clay minerals would have on sorption behaviour would be masked.

Similarly Hodgson et al. (1969) pretreated soil clay minerals with hydrogen peroxide to remove organic matter and manganese oxides to some extent. They also used Li oxalate/Na oxalate mixture to remove iron oxide coatings without affecting the clay surface structure. The reactivity of 4 out of the 7 minerals to cobalt was increased by iron removal, implying that in these cases the surfaces exposed were more reactive than the iron oxide coating. The clay fraction of one soil, a fine sandy loam, was principally of kaolin and was more reactive than clay fractions containing principally montmorillonite. However, results from cobalt sorption on geological minerals demonstrated that montmorillonite had a higher sorption capacity than kaolinite.

Hodgson (1960) studied, in detail, the nature of the specific reactions of cobalt with montmorillonite using the radioisotope cobalt-58 as tracer. He demonstrated that acid pretreatment of montmorillonite decreased its ability to sorb cobalt, even although the solution pH was readjusted to the original value. Using 0.1 N $CaCl_2$, with or without non-radioactive cobalt, cobalt-58 was desorbed from the mineral and from the results Hodgson postulated that there were at least two specific exchange reactions or two groups of reactions taking place. He then went on to separate the exchangeable and non-exchangeable forms of specifically-sorbed cobalt, using 2.5% acetic acid solution.

Further investigations were carried out by Hodgson, Geering and Fellows (1964) who noted that pretreatment of montmorillonite with NH_4F caused a decrease in the sorption capacity of the clay mineral. They suggested that there was replacement of the surface hydroxyls by fluoride to which cobalt was only weakly bound. The proposal that cobalt was bound to the surface hydroxyl groups is of interest with respect to the results of de Mumbrum and Jackson (1956), who reported that the surface-hydroxyl infra-red absorption peaks of montmorillonite, vermiculite, and kaolinite were decreased by surface saturation with copper and zinc ions. The absorption peak was due to octahedral hydroxyl groups in the layer silicates of the minerals.

The effect of temperature on the reaction of cobalt with montmorillonite was also measured by Hodgson, Geering and Fellows (1964) who showed that an increase in the ambient temperature promoted sorption of cobalt. Thus the reaction was endothermic and the authors accounted for this by concluding that the cobalt was exchanging for a more strongly bound ion, such as weakly dissociable H^+. This was in contrast to the results of Singhal and Singh (1973) who, by exchanging cobalt for sodium on montmorillonite, noted a decrease in enthalpy. However, the solution cobalt concentration was considerably higher than that used by Hodgson et al. (1964). Thus the reaction was principally one of cation exchange at charged sites on the mineral.

The latter authors also investigated the effects of solution calcium on the specific sorption of cobalt to montmorillonite. They reported that when the cobalt level in solution was expressed in terms of concentration, a decrease in the amount of Co sorbed resulted from increasing the calcium concentration, but this change could be eliminated by expressing the Co levels in terms of chemical activity. They proposed that increasing calcium concentration caused the Co activity in the bulk solution to be lowered consequently decreasing the amount of cobalt able to sorb onto the solid.

The effect of solution alcohol on cobalt sorption was also studied. This eliminated any effects on sorption due to hydrolysis of the cation. There was in fact an enhancement of sorption, especially at solution alcohol concentrations above 60%. The authors concluded that the alcohol had promoted changes in the surface structure of the mineral, so enhancing its sorption capacity for cobalt and that if the hydrolysed ion was adsorbed by the mineral then the surface effects more than compensated for the decrease in cobalt hydrolysis in solution.

Sorption of copper and zinc by montmorillonite was shown to be almost equivalent to cation exchange at pH 2.2-2.5 (Bingham et al. 1964). Results from pH and solubility effects indicated that, above pH 6.0, there was excess retention of the metals caused by precipitation in the clay system.

Maes and Cremers (1975) noted that low and intermediate occupancy of cobalt on montmorillonite was perfectly reversible up to pH 6.0. However, at higher occupations of cobalt, a significant portion of the sorbed cobalt became irreversibly fixed. The range of solution cobalt concentration in this experiment was considerably higher than those used in the aforementioned studies on montmorillonite. Thus the irreversibly-fixed portion of the sorbed cobalt was probably due to surface precipitation of the hydroxide.

Peigneur et al. (1975) again noted no specific sorption at low surface coverage and postulated that there were two different regions of charge density on montmorillonite: a pH insensitive fraction at the basal layers of the mineral and a pH sensitive fraction at the clay edge. Both fractions were thought to be involved in cobalt sorption.

The solution cobalt concentrations used were higher than those likely to be encountered in the soil.

The role of hydrolysis of the cobaltous cation in solution was further investigated by Hodgson, Tiller and Fellows (1964). The specific sorption of cobalt tagged with cobalt-58 on several minerals was studied in the presence of Mg^{2+}, a weakly competing ion, against solution pH. The results were consistent with the adsorption of hydrolysed ionic cobalt ($Co(OH)^{+}$). This was in contrast to the results of Hodgson, Geering and Fellows (1964) which suggested that hydrolysis was probably not important in Co sorption by montmorillonite. Spencer and Gieseking (1954), using the radioisotope cobalt-60, measured the

exchangeability of cobalt on the cation exchange resin Amberlite as well as on montmorillonite and an illitic clay. Cobalt was more difficult to replace than calcium on the Amberlite and montmorillonite. However, with the illitic clay there was no difference in their exchangeability.

The authors also observed that a relatively large proportion of cobalt appeared to be adsorbed on calcium-saturated Amberlite as the hydroxy-cobaltous ion, and suggested that both Co^{2+} and $Co(OH)^{+}$ were being adsorbed. With hydrogen saturated Amberlite, equivalent amounts of cobalt were adsorbed and H^{+} released, the pH of the reaction medium probably being too low for the hydrolysis of Co^{2+}.

1.5.3 SORPTION ON SOIL OXIDES

The reactions of cobalt with soil oxides have already been briefly mentioned in the context of clay mineral surface coatings. A number of authors have attempted to elucidate the nature of the bonds formed between cobalt and the 'free' soil oxides; these being of an amorphous or slightly crystalline nature. Relatively few of these studies, however, have used oxides extracted from soil.

In Australia, McKenzie (1967) extracted manganiferous nodules, containing the minerals birnessite, lithiophorite, and hollandite, from soil and sorbed cobalt, copper and nickel onto these in the presence of 0.1 N $CaCl_2$ in order to eliminate non-specific sorption. Differentiation of extractable and non-extractable fractions was carried out using 2.5% acetic acid solution. The resultant sorption

isotherms showed the sorption of copper to be much greater than cobalt or nickel. With all 3 elements, there was a drop in pH although the amount of H^+ released was equivalent to only about 0.5 per cent of the quantity of metal sorbed. Cobalt sorption released more manganese into solution than copper or nickel and acetic acid extraction of the sorbed metals indicated that cobalt was the most strongly bound.

The removal of manganese from the minerals using acidified hydrogen peroxide considerably reduced the amounts of both cobalt and copper sorbed and aging of the mineral caused the amount of non-extractable cobalt to increase dramatically until after 180 days, 86 per cent of the cobalt originally extracted had become non-extractable by acetic acid. This phenomenon was not observed with copper or nickel. Desorption of the sorbed metals into solution showed that the reactions were only partially reversible.

The authors concluded that there was probably slow diffusion of cobalt into the oxide crystal lattice with subsequent incorporation into the structure.

In some soils, most of the cobalt has been shown to be associated with manganese minerals (Taylor, 1968; Taylor and McKenzie, 1966).

Using laboratory prepared minerals, McKenzie (1970) studied the sorption of cobalt, copper and nickel on birnessite, cryptomelane, β-MnO_2 and pyrolusite. The ability to replace K^+ from the minerals was in the order Cu > Co > Ni; however the ability to replace manganese was Co > Cu > Ni, except in pyrolusite, where there was little

difference between copper and cobalt. The authors maintained that substitution of lower valence manganese for Mn^{4+} is a common feature of all higher oxides of manganese, except pyrolusite, and that cobalt was replacing the lower valence manganese in these oxides. It was postulated that after surface adsorption of Co^{2+}, it begins to diffuse into the surface layers of the crystal lattice where it is oxidised and replaces Mn^{3+}. This oxidation-reduction reaction is favourable thermodynamically according to the theory of crystal field stabilisation energy. It is not favourable in the cases of copper or nickel. In soils, the displaced Mn^{2+} would probably remain on the surface of the oxide, because of the oxide's highly charged nature, and reoxidation of the manganese would build it back into the lattice.

It must be emphasised that the above author used solution cobalt concentrations far in excess of those likely to be encountered in the soil. However, in the soil, over a period of time, there may be a build up of cobalt in manganese oxides by the mechanism described.

Loganathan et al. (1977), using laboratory prepared amorphous δ-MnO_2, carried out cobalt sorption with varying solution pH. Again the cobalt concentrations used were greater than those likely to be encountered in the soil. As with McKenzie (1970) cobalt sorption was found to displace Mn^{2+} into solution, although far less was replaced by an equivalent uptake of Zn^{2+}. The authors proposed that, at solution pH values below 5, Co^{2+} interchanged with both Mn^{2+} and Mn^{3+} in the δ-MnO_2 structure and Zn^{2+} interchanged

only with Mn^{2+}. At solution pH values greater than 6, there was an abrupt increase in cobalt sorption. The mechanism suggested for this large quantity of cobalt sorption was that as initially cobalt is adsorbed onto the oxide, the surface charge becomes positive, attracting hydroxyl anions, which precipitate cobalt on the surface as cobalt hydroxide.

Measurements of cobalt sorption on iron, manganese and aluminium oxides as a function of pH have shown iron and manganese oxides to have significantly higher sorption capacities for cobalt than aluminium oxide as measured from the Langmuir isotherm (Tewari et al. 1972).

Specific sorption of trace metals onto goethite was measured as a function of pH by Forbes et al. (1976). Affinity for the goethite surface was in the order Cu > Pb > Zn > Co > Cd, and the sorption curves were considered to be influenced by surface charge, adsorption density of the ions and their size.

In the less crystalline system of amorphous iron oxyhydroxide, Benjamin and Leckie (1981) concluded that metal cation adsorption was at heterogeneous sites with variable bonding energy. From their own results and those of other workers, these authors calculated that the adsorption densities on amorphous ferric oxide increased in the order: Pb, Ag, Cd < Cu < Hg < Zn < Co.

Although not strictly comparable with the results of Forbes et al. (1976), it would be expected that the adsorption density would depend on the affinity of the oxide surface for the metal ion. The positionings of cobalt with

respect to other metals in the two series above are remarkably dissimilar, indicating possibly that in the more crystalline system (goethite), ionic size plays a major role for adsorption into the crystal lattice. In the more amorphous system the chemical nature of the ionic species is probably of more importance in relation to its ability to substitute for iron in the oxide.

James and Healy (1972a) sorbed cobalt onto amorphous SiO_2 and TiO_2 at varying solution pH. Sorption and hydrolysis of the cation were not found to be directly related although there was a general qualitative relationship between the pH at which there was an abrupt increase in adsorption, and the pH of hydrolysis of Co^{2+}.

1.5.4 SORPTION ON ORGANIC MATTER

The results from a number of trials on the application of cobalt to soil indicated that organic matter may initially fix cobalt added to the soil. This fixation has been studied by Beckwith (1955) who measured the change in pH of three organic soils following the addition of metals from the first transition series. The extent of decrease in soil pH caused by metal ion addition followed the sequence Cu > Ni > Co > Mn and was in accordance with the Irving-Williams stability constant series based on metal-ligand formation using various chelating agents.

Stevenson and Ardakani (1972) calculated the stability constants for metal-soil organic matter complexes and found them to be lower than those for complexes of the same metal ions with commercial chelating agents such as EDTA.

The interaction between the humic acid fraction of soils and metal cations indicated that there was metal-humate complex formation (Khan, 1969). By titrating the humic acid against base in the presence of metallic ions and observing the amounts of cations required to coagulate the humic acid, a metal ion stability series was obtained similar to that of the Irving-Williams series.

Schnitzer and Skinner (1967), working with the lower molecular weight fulvic acid, calculated metal-fulvate stability constants at two pH values. All the stability constants were higher at pH 5.0 than 3.5 and the authors ascribed this to increased ionisation of functional groups on the fulvic acid, especially the carboxyl groups. The position of cobalt in the stability series obtained did not differ greatly from its position in the Irving-Williams series indicating, again, that cobalt is associated with soil organic matter through the formation of complexes.

Indirect evidence for the type of complexes formed comes from infra-red wavelength absorption studies on peat after saturation with copper and zinc. There were numerous shifts in the absorption wavelength of the double bond region which was indicative of chelation with carbonyl and nitrile groups in the molecular structure of the peat (de Mumbrum and Jackson, 1956b).

The possibility of organically complexed cobalt being present in the soil solution was investigated by Hodgson et al. (1965) in 4 soils from New York State in the USA, using a

ligand partition system. Cobalt was complexed to a very limited degree compared to copper, but to a similar extent as zinc. In all cases, the percentage of the ionic species complexed was higher in the soil solutions from the surface horizons.

CHAPTER 2. MATERIALS AND METHODS

2.1 Analysis of soils

All soil samples for analysis were air dried and roll milled, through a stainless steel mill, to a particle size less than 2 mm.

2.1.1 PARTICLE SIZE ANALYSIS was carried out by sieving and sedimentation techniques (Ministry of Agriculture, Fisheries and Food, 1973).

2.1.2 ORGANIC CARBON was measured by oxidising the soil organic matter with dichromate and titration of unreduced dichromate with standard $FeSO_4$ solution according to the method of Walkeley-Black (Allison, 1965).

2.1.3 CATION EXCHANGE CAPACITY was measured by the method described by Bascomb (1964).

2.1.4 SOIL pH

The pH of the soils in aqueous suspension was obtained from a 40g sample of soil (< 2 mm particle size) in a polythene beaker, to which 100 ml deionised water were added. The contents were stirred and allowed to stand for one hour before being restirred. The pH of the soil-water suspension was then measured using a glass electrode with a calomel reference electrode.

Analysis of the final solution for cobalt was carried out by atomic absorption spectrophotometry using a carbon rod atomiser.

2.1.5 NITRIC-PERCHLORIC ACID DIGEST

To a 4g sample of finely ground soil in a 100 ml Pyrex beaker 30 ml of acid digestion mixture were added (4 vols, 70% HNO_3: 1 vol, 70% $HClO_4$). A watch glass was placed on the beaker and the contents heated on a sandbath until fumes of perchloric acid were visible. After heating for a further 20 minutes, the watch glass was removed and the contents brought to dryness. After cooling, 15 ml of 6N HCl were added and the acid digest of the soil heated to dryness on the sandbath. A 10 ml volume of 1.5N HCl was then added and the soil digested under a watch glass for 15 minutes. The contents of the beaker were filtered hot into a 50 ml volumetic flask through a 9 cm Whatman's No. 40 filter paper. The beaker and filter paper were washed with distilled water and the washings added to the flask. The sample was diluted to volume using distilled water.

The final solution was analysed for cobalt, iron and manganese by flame atomic absorption spectrophotometry.

2.2 Extractable and isotopically exchangeable soil cobalt

2.2.1 0.5 M ACETIC ACID EXTRACTABLE COBALT

100 ml of 0.5 M acetic acid solution were added to 6g of soil (<2 mm particle size) in a 150 ml polypropylene centrifuge tube. The contents were shaken for 16 hours on a rotary shaker, with the long axes of the tubes moving in a direction perpendicular to the motion of the shaker. This conferred a rolling action on the tubes and contents.

The contents were then filtered through a 15 cm Whatman's No. 42 filter paper into a polythene bottle.

Analysis of the filtrate for cobalt was by atomic absorption spectrophotometry using a carbon rod atomiser (see 2.4.2).

2.2.2 0.04 M DISODIUM EDTA EXTRACTABLE COBALT

An 8g sample of soil (<2 mm particle size) was shaken for 16 hours with 40 ml 0.04 M di-sodium EDTA solution in a 100 ml polypropylene centrifuge tube on a rotary shaker as in the method used for acetic acid extractable soil cobalt. This was carried out in an incubator at 20°C. The tubes were then centrifuged at 6,000 rpm for 10 minutes. 20 ml of the supernatant were pipetted into a 150 ml beaker and evaporated to dryness on a sandbath. The beaker was cooled, 4 ml 70% HNO_3 and 1 ml 70% $HClO_4$ were added and covered with a watch glass. The contents were heated until perchloric acid fumes appeared and the heating was continued until the contents were nearly dry. The beaker was allowed to cool before the addition of 5 ml 3N HCl and taking to dryness. A volume of 10 ml 0.5 M acetic acid was then added and the residue allowed to dissolve before the solution was poured into a 30 ml glass, stoppered centrifuge tube. The beaker was washed twice with 5 ml acetic acid solution and the washings added to the centrifuge tube.

Analysis of the final solution for cobalt was by atomic absorption spectrophotometry using a carbon rod atomiser (see 2.4.2).

2.2.3 ISOTOPICALLY EXCHANGEABLE COBALT

To 4.0g samples of finely ground soil (particle size <2 μm), in 50 ml polypropylene centrifuge tubes, 20 ml of 0.05 M $CaCl_2$, adjusted to pH 6.0 using saturated $Ca(OH)_2$ solution, were added. The tubes were stoppered and shaken in a rotary shaker for 48 hours. They were then centrifuged at 3,000 rpm for one minute and the supernatant solution shaken up to the lid in order to dislodge any particles of soil trapped between the stopper and wall of the vessel. The tubes were then recentrifuged at 6,000 rpm for 10 minutes and, using a 'Gilson' automatic pipette, 0.1 μCi carrier-free cobalt-58 in 0.01 ml 0.05 M $CaCl_2$ solution was added. The supernatant was gently shaken to disperse the radioisotope throughout the solution and then there was vigorous shaking of the tubes to dislodge the centrifugate at the bottom of the tubes. The cobalt-58 was allowed to exchange with the non-radioactive cobalt present in the system by shaking in the rotary shaker for a further 48 hours. The tubes were then centrifuged twice, as before, but the second centrifugation lasted for 20 minutes. Using a 'Gilson' pipette, 2 ml samples were taken from the supernatant and pipetted into glass phials for radioactivity measurement by scintillation counting. This was carried out using a Panax, Reigate Series, well-type scintillation counter equipped with a sodium iodide crystal containing thallium impurity. The activity of a 2 ml sample of solution, which had not been shaken with soil, was also measured.

A further 10 ml of supernatant was pipetted into a 30 ml glass stoppered centrifuge tube for cobalt analysis by carbon-rod atomic absorption spectrophotometry. This was carried out as described in section 2.4.2 but using only half of the stated volumes of reagents.

The isotopically exchangeable cobalt concentration $[Co_{ie}]$ was calculated from the equation:

$$[Co_{ie}] = [Co_{soln}] \times \frac{(^{58}Co \text{ original activity}) - (^{58}Co \text{ final activity})}{(^{58}Co \text{ final activity})}$$

Cobalt-58 is a beta and gamma-ray emmitter with a half-life of 71 days. Activity thus remains adequately high for measurement in experimental periods lasting several days.

The pH values of the supernatant solutions were measured using a Pye-Unicam, Model 290 Mk 2 pH meter equipped with a combined glass/calomel electrode.

2.2.4 CALCIUM CHLORIDE EXTRACTABLE SOIL COBALT

The 0.05 M $CaCl_2$ extractable soil cobalt was the quantity $[Co_{soln}]$, in the isotopically exchangeable cobalt measurements.

2.3 Analysis of herbage

Herbage samples were dried at 110°C and milled, using either a steel herbage mill for large field samples or a coffee bean grinder for smaller samples.

2.3.1 COBALT CONTENT

A 5g sample of herbage was weighed into a silica basin, dried at 80°C for 2 hours, and reweighed. It was then ashed in a muffle furnace at 450°C overnight and when cool, 5 ml concentrated HNO_3 added and taken to dryness on a

steambath. The digest was then re-ashed at 450°C for 2 hours and, when cool, 10 ml 6N HCl were added and taken to dryness. Approximately 20 ml of 3N HCl were added and a watch glass placed on the basin. The contents were then digested for 15 to 20 minutes. The residue was filtered through an 11.0 cm Whatman's No. 541 filter paper into a 150 ml Pyrex beaker. The surfaces of the basin and paper were washed with hot distilled water into the beaker and the solution taken to dryness on a hot plate. Exactly 15 ml 0.5 M acetic acid was pipetted into the beaker and the residue allowed to dissolve before pouring the contents into a 30 ml glass, stoppered centrifuge tube. The beaker was washed with exactly 5 ml acetic acid solution and the washings poured into the centrifuge tube.

Analysis of the final solution for cobalt was by atomic absorption spectrophotometry using a carbon rod atomiser.

2.4 Cobalt analysis by atomic absorption spectrophotometry

2.4.1 FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

The analysis of soils treated with nitric-perchloric acids was carried out using a Varian Techtron AA5 atomic absorption spectrophotometer with an air/acetylene flame.

The absorbance of cobalt was measured at a wavelength of 240.7 nm.

The absorbance value of the sample was compared with those of sets of standard solutions prepared in 0.01 N HCl.

2.4.2 ATOMIC ABSORPTION SPECTROPHOTMETRY USING A CARBON ROD ATOMISER

The analysis of soil acetic acid, EDTA and calcium chloride extracts, cobalt sorption equilibrium solutions and

solutions from the herbage digests, was by flameless atomic absorption after a solvent extraction procedure had been carried out on the sample solutions. This was based on the method of Mountjoy (1970).

To 20 ml samples of solution in 30 ml glass, stoppered centrifuge tubes, 1 ml H_2O_2 (10 vol) was added followed by 1 ml 40% $^{w}/v$ sodium citrate solution. The tubes were briefly shaken before 1 ml of 2 nitroso-1-naphthol in glacial acetic acid (1% $^{w}/v$) was added. The tubes were shaken again and after being allowed to stand for 30 minutes, 5 ml of 4 methyl pentan-2-one (MIBK) were added and the tubes shaken vigorously for 2 minutes. Samples were taken from the top (organic) phase for analysis.

A range of standard cobalt solutions in 0.5 M acetic acid were prepared with concentrations ranging from 0.004 ppm to 0.4 ppm Co. These were extracted into MIBK by the method described above.

Where cobalt concentration in the aqueous solution was low the concentration of cobalt in the organic phase could be increased by shaking the aqueous solution with a smaller volume of MIBK.

Analysis of the organic phase for cobalt concentration was conducted using a Varian Techtron AA5 atomic absorption spectrophotometer fitted with a Model 63 carbon rod atomiser. 5 µl of sample were injected into the rod either manually, using a Hamilton 20 µl syringe, or by a Model ASD-53 automatic sample dispenser.

The conditions used for the atomisation of cobalt were:-

drying - voltage setting 3 for 26 seconds
ashing - voltage setting 7 for 15 seconds
atomisation - voltage setting 7 for 3 seconds

The voltage settings are equivalent to about 100°C, 700°C and 2,200°C for drying, ashing and atomisation respectively.

2.5 Iron and Manganese analysis by atomic absorption spectrophotometry

Analysis for iron and manganese was carried out on the nitric-perchloric soil digests using flame atomic absorption spectrophotometry after suitable dilution of the final solution. The methods were similar to that used for cobalt. The absorbances of iron and manganese were measured at wavelengths of 248.3 and 279.5 nm respectively.

CHAPTER 3.

THE EFFECT OF TEMPERATURE, TIME AND SOIL-SOLUTION RATIO ON THE EXTRACTABILITY OF SOIL COBALT BY 0.5 M ACETIC ACID

Acetic acid (ethanoic acid), either as a 0.5 M or 2.5% solution (0.42 M), has been used extensively as a routine extractant for plant available soil cobalt. Usually this has involved an overnight shaking of the soil with the extractant and the subsequent measurement of the concentration of cobalt brought into solution.

Very few, if any, results have been published on the effects that a change in the conditions used may have on the amount of cobalt extracted from the soil. It is probable that in an analytical laboratory the ambient temperature will vary and that the period of extraction will not be consistent from day to day. It was therefore considered that a study of these variables would be of interest.

The following experiments were designed to measure the effects of varying the extraction period, ambient temperature and soil to solution ratio on the amount of cobalt brought into solution. Variations in the amount of cobalt extracted were compared with the amounts of iron, manganese and organic matter extracted.

3.1 Experimental Method

3.1.1 THE EFFECT OF AMBIENT TEMPERATURE ON COBALT EXTRACTABILITY

Three soils were used. The soils were topsoil samples obtained from the Borders region of Scotland. Soil 36 was of the Hobkirk soil series with a pH, in water, of 5.9. Soils 39 and 57 were of the Linhope series with pH values of 5.4 and 4.8 respectively.

Samples of soil, weighing 5.0g, (<2 mm particle size) were placed in 150 ml polypropylene centrifuge tubes followed by 100 ml of 0.5 M acetic acid. The contents were shaken in a rotary shaker inside an incubator for 16 hours at ambient temperatures ranging from 5^{o} to 30^{o}C. The extracts were filtered through 15.0 cm Whatman's No. 42 filter paper into polythene bottles. These were stored in a fridge before analysis for cobalt by atomic absorption spectrophotometry using a carbon rod atomiser. Iron and manganese in solution were analysed by flame atomic absorption spectrophotometry by the method described in section 2.5.

The amount of organic matter extracted by 0.5 M acetic acid solution was estimated by measuring the optical absorbance of the extracts at a wavelength of 400 nm using a Unicam SP 600 Series 2 U.V spectrophotometer.

3.1.2 THE EFFECT OF THE DURATION OF THE EXTRACTION ON COBALT EXTRACTABILITY

Two of the soils used in the temperature experiment (nos, 36 and 57) were studied. Samples of soil (5.0 g) were shaken with 100 ml 0.5 M acetic acid as in the temperature experiment. The ambient temperature was maintained at 20^{o}C. The period of extraction was varied from one to 48 hours. Cobalt, iron and manganese concentrations were measured in solution as described previously.

3.1.3 THE EFFECT OF SOIL-SOLUTION RATIO ON COBALT EXTRACTABILITY

Only one of the soils used previously (no. 36) was studied in this experiment.

Soil samples varying in weight from 2.5g to 10g were shaken, as described previously, with 100 ml 0.5M acetic acid at 20°C for 16 hours. Cobalt concentration in solution was measured as described previously.

3.2 Results and Discussion

Figures 3.1 to 3.3 demonstrate the increase in extractability of soil cobalt by 0.5 M acetic acid with increasing ambient temperature. The rate of increase was especially high around a temperature of 20°C, room temperature, so that a fluctuation in the air temperature of an analytical laboratory between extractions could markedly affect the amount of cobalt solubilised in a soil. In soil 39 an increase in temperature from 15°C to 25°C increased the concentration of cobalt brought into the acetic acid by 45 per cent. A soil deemed to be of borderline deficiency (0.3 ppm extractable Co) at the lower temperature would appear to contain sufficient extractable cobalt at the higher ambient temperature.

It is notable also that the amount of iron and manganese brought into solution increased with temperature in parallel to the extractable cobalt.

Assuming soil no. 39 contained fairly typical concentrations of total Co, Fe and Mn, these being 8 ppm, 20,000 ppm and 500 ppm respectively, then as the ambient temperature increased from 5°C to 30°C, the percentage of the total Co extracted increased from 4 to 12 per cent; Fe from 0.06 to 0.15 per cent; and Mn from 10 to 21 per cent.

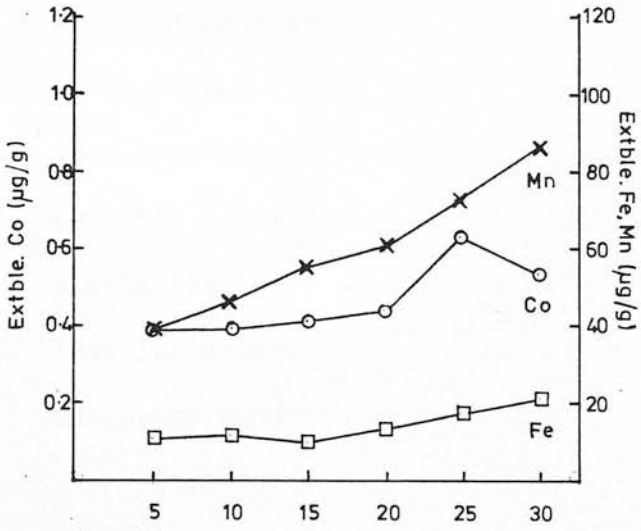


FIG. 3.1

Relationship between extractable soil Co, Fe, Mn and ambient temperature. SOIL 36

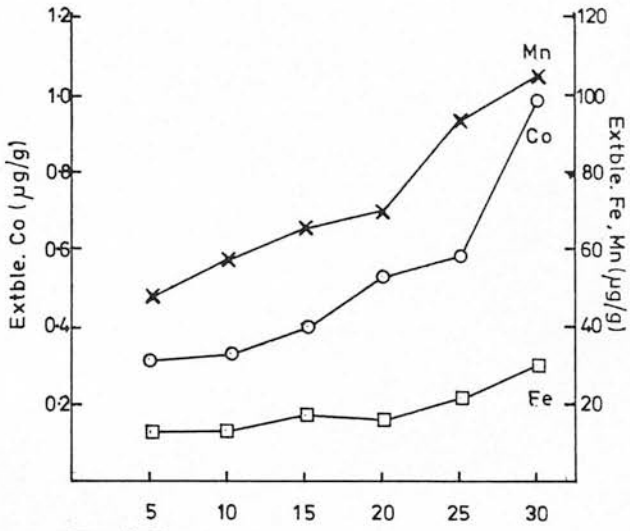


FIG. 3.2

Relationship between extractable soil Co, Fe, Mn and ambient temperature. SOIL 39

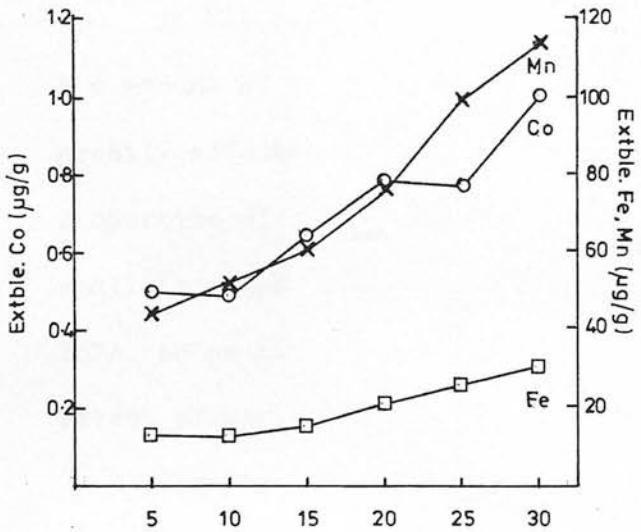


FIG. 3.3

Relationship between extractable soil Co, Fe, Mn and ambient temperature. SOIL 57

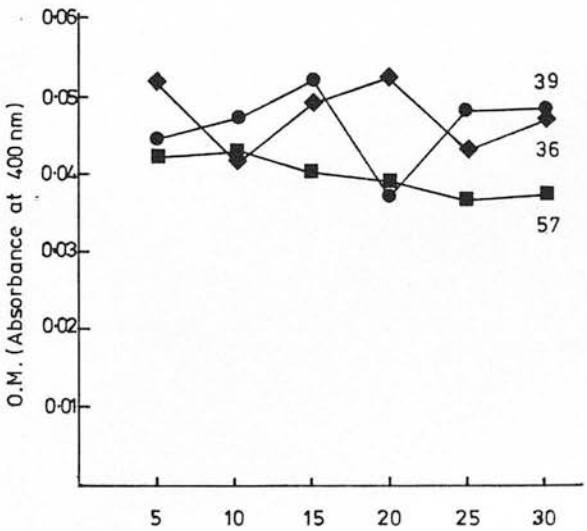


FIG. 3.4

Absorption characteristics of extraction solutions at 400 nm in relation to ambient temperature. SOILS 36, 39, 57

The percentage of the soil cobalt solubilised was similar to that of manganese. Since 0.5 M acetic acid has a pH of 2.5 it would be expected that a portion of the soil oxide fraction would be dissolved during the extraction, especially the material of a less crystalline nature. Thus most of the Fe and Mn in solution probably was derived from their amorphous oxides. The close similarity in behaviour between cobalt and manganese suggests that the extractable cobalt was strongly associated with the manganese oxides.

This does not preclude the possibility that, although only a small percentage of the total iron content was extracted, a very high proportion of the soil cobalt was incorporated with the amorphous iron oxide fraction, thus causing the observed results. The possibility also exists that the cobalt was associated with the amorphous aluminium oxide material which would also be solubilised by the acetic acid.

In Figure 3.4, the solution absorbance at 400 nm shows that the amount of organic matter solubilised by acetic acid was not greatly affected by the temperature of extraction. The actual proportion of soil organic matter dispersed by acetic acid is small in comparison to that of other soil extractants such as EDTA, so no conclusions can be drawn from this result as to the extent of the association of cobalt with soil organic matter.

Figures 3.5 and 3.6 show the large effect that the period of extraction had on cobalt extractability. In the case of soil no. 57 the rate of increase in extractability was particularly high at around the 16 hour extraction period. The extractable iron and manganese concentrations again increased in parallel with that of cobalt.

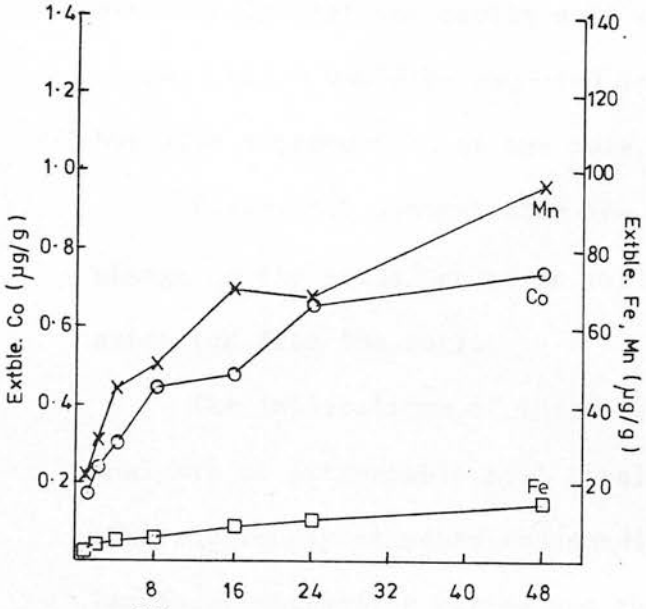


FIG. 3.5 Relationship between extractable soil Co, Fe Mn and period of extraction. SOIL 36

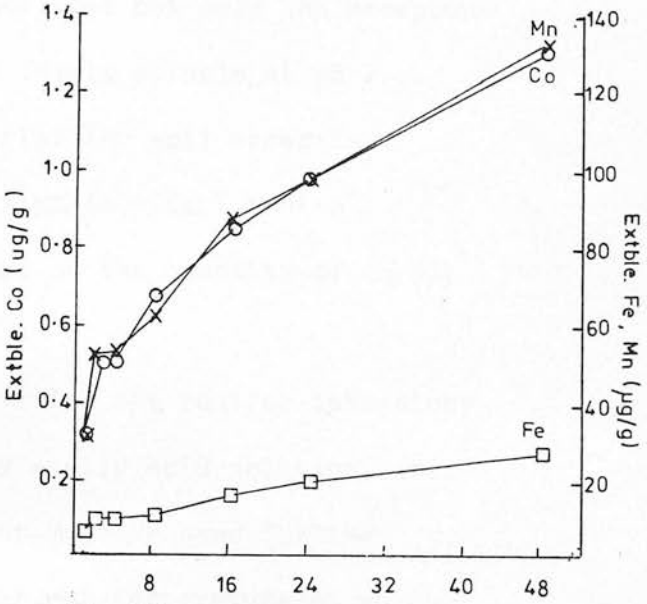


FIG. 3.6 Relationship between extractable soil Co, Fe Mn and period of extraction. SOIL 57

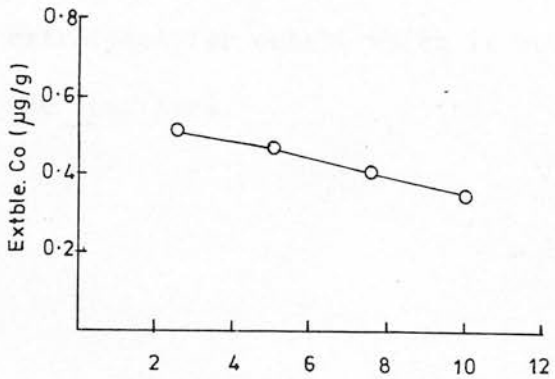


FIG. 3.7 Relationship between extractable soil Co and soil : solution ratio. SOIL 36

It is of note that at the 48 hour extraction period, the extractable metal concentrations were still increasing, this being especially marked with Mn and Co. From this, it would seem likely that the acetic acid solubilised not only the amorphous oxides, which would be expected to be fairly soluble at pH 2.5, but also a proportion of the more crystalline soil minerals.

Figure 3.7 demonstrates the negligible effect that a change in the soil: solution ratio had on the quantity of cobalt extracted from the soil.

The implications of these results for the routine laboratory analysis of extractable soil cobalt by acetic acid solution, are that rigorously standardised conditions must be used for the length of extraction period and the ambient temperature at which it is carried out. The fact that the cobalt extracted by acetic acid appears to be incorporated into the oxide fraction of the soil suggests that most of the cobalt will not be plant available, and would only become soluble or easily exchangeable after reduction of the soil oxides. Thus 0.5 M acetic acid may prove to be a more suitable soil extractant for cobalt which is potentially available for plants in the long term.

CHAPTER 4.

THE TOTAL, EXTRACTABLE AND ISOTOPICALLY EXCHANGEABLE COBALT IN SOILS FROM SOUTH-EAST SCOTLAND

A number of soil extractants have been used to estimate the quantity of plant-available cobalt in soils and to examine the association of cobalt with individual soil components. The latter aim has been pursued by Kubota (1965) who observed that the amount of soil cobalt extracted by acetic acid increased with the amount extracted by dithionite. This was taken as an indication that cobalt was associated with the soil iron oxides. The quantity of cobalt extracted by 2.5% acetic acid has also been found to be correlated with the soil clay content (Rana and Ouellette, 1967). Le Riche and Weir (1963) observed that there was an enrichment of soil cobalt in the ammonium oxalate-extractable fraction of the soil and took this as evidence for cobalt's association with iron oxides in the soil. Similarly, evidence for the association of cobalt with the free oxides in the soil was obtained by Rerikh et al. (1975) using Tamm's acid oxalate as extractant.

McLean and Langille (1976) made the observation that 0.1 N HCl extractable cobalt increased with soil organic matter and clay content of the soil.

In order to measure the amounts of cobalt associated with the solid phase of the soil, which are exchangeable with solution cobalt, isotopic exchange methods have been used. Tiller et al. (1969) showed that soils with the largest proportion of cobalt which was isotopically exchangeable had the lowest total cobalt contents. For the majority of the soils studied the isotopically exchangeable cobalt appeared to be derived from easily exchangeable cobalt and

cobalt sorbed on the manganese oxides.

In the present experiment 3 soil extractants were used:

0.5 M acetic acid, 0.04 M EDTA and 0.05 M $CaCl_2$

Acetic acid is commonly used as a soil extractant for 'available' soil cobalt. EDTA is commonly used as a soil extractant for copper. As a chelating agent it is able to complex copper associated with the soil organic matter. Mitchell (1972) also used 0.05 M EDTA to extract cobalt from the soil organic matter. Calcium chloride was used in this experiment to extract cobalt from soil solution and on the cation exchange sites.

Isotopically exchangeable cobalt was also determined as a measure of the amount of labile soil cobalt.

These quantities were measured in 20 soils from South-East Scotland and compared with soil properties such as pH, C.E.C., and manganese and iron oxide contents.

4.1 Experimental Method

4.1.1 SOILS

Samples from the top 20 cm of 20 soils in the Lothian and Borders regions of Scotland were collected. These were sieved, in a moist state, through a 6.5 mm sieve and stored in sealed polythene bags. Chemical and physical analyses were carried out on soil samples, as described in section 2.1.

4.1.2 EXTRACTABLE AND ISOTOPICALLY EXCHANGEABLE COBALT

The concentrations of soil cobalt extracted by 0.04 M di-sodium EDTA and 0.05 M $CaCl_2$ were measured by the methods described in sections 2.2.2 and 2.2.4.

The 0.5 M acetic acid soil cobalt extraction is described in section 2.2.1, but was carried out at 20°C in this

experiment. Isotopically exchangeable cobalt concentration was measured by the method described in section 2.2.3.

4.2 Results and Discussion

The results of the soil analyses are present in Table 4.1. Descriptions of the soil series can be obtained in the relevant memoirs of the Soil Survey of Great Britain (Ragg, 1960; Ragg and Futty, 1967).

Table 4.1. Analyses of Soils

Soil No	Soil Series		% clay	% org C	C.E.C m equiv/ 100g	nitric/perchloric acid digest Mn (µg/g)	Fe (%)	Co (µg/g)	pH (H_2O)
1	Eckford	a	10.8	2.6	16.4	220	0.91	4.15	6.9
2	Kedslie	a	20.5	2.1	17.5	410	2.18	11.75	7.4
3	Kedslie	a	24.1	3.2	21.1	510	2.51	13.61	6.0
4	Sourhope	a	19.2	3.4	21.3	380	1.85	10.71	6.0
5	Hobkirk	a	20.4	2.6	20.8	430	2.24	12.68	6.1
6	Ettrick	a	26.6	3.5	17.6	550	2.57	14.08	6.8
7	Eckford	a	15.9	1.9	13.8	170	1.24	7.31	7.1
8	Cessford	a	24.1	4.9	28.4	220	2.28	8.85	5.7
9	Sourhope	a	16.5	3.3	23.9	370	1.91	9.42	5.9
10	Belses	a	29.2	2.1	20.9	470	2.66	14.50	6.2
11	Hobkirk	a	21.2	2.3	17.1	310	2.08	11.99	6.7
12	Lauder	a	23.2	2.6	20.5	510	2.17	11.53	6.7
13	Basin Peat	c a	20.1	5.4	22.9	140	0.87	5.10	6.9
14	Eckford	a	18.5	4.4	22.8	220	2.72	11.41	6.4
15	Eckford	a	20.0	3.8	25.7	540	3.09	20.99	5.9
16	Eckford/ Hobkirk	a	15.6	5.6	22.0	150	0.88	3.89	5.1
17	Andesitic Drift	b	23.4	2.7	23.8	550	2.93	15.80	6.4
18	Winton	b	21.6	2.7	17.2	230	2.70	11.25	6.0
19	Darvel	b	18.7	2.7	18.3	520	2.34	13.04	6.2
20	Alluvial	b	12.3	1.7	15.9	230	1.49	6.08	5.8

a. Ragg, (1960)
b. Ragg and Futty, (1967)

Brief descriptions of the soils are given in Appendix Y on page 251.

c. According to soil map. Analysis indicates mineral soil.

4.2.1 TOTAL COBALT CONTENT

The soils were analysed for cobalt, iron and manganese using a nitric acid - perchloric acid soil digest. Although this is a powerful oxidising agent it is unlikely to release any cobalt present in the primary silicate minerals. This latter fraction is unlikely to constitute a significant proportion of the total soil cobalt content, especially in the soils derived from Old Red Sandstone and Andesitic lavas.

Total soil cobalt concentration was significantly correlated with soil clay content ($r = 0.63$, $P < 0.01$) and with the concentrations of iron ($r = 0.91$, $P < 0.001$) and manganese ($r = 0.83$, $P < 0.001$) dissolved by nitric/perchloric acid (Figs. 4.1 and 4.2). It is assumed that this reagent dissolves manganese and iron from their oxides and hydroxides with a small percentage from the soil organic matter. The association between soil cobalt content and soil oxides has also been reported in the literature. Taylor and McKenzie (1966) dissolved the manganese oxides birnessite and lithiophorite from some Australian soils and found that, on average, 79 per cent of the soil cobalt was associated with these minerals. McKenzie (1975), using an electron microprobe, found 30-53 per cent of the total soil cobalt to be associated with manganese oxides.

The association of cobalt with soil iron oxides has been reported by Le Riche and Weir (1963), Kubota and Lazar (1960) and Rerikh et al. (1975).

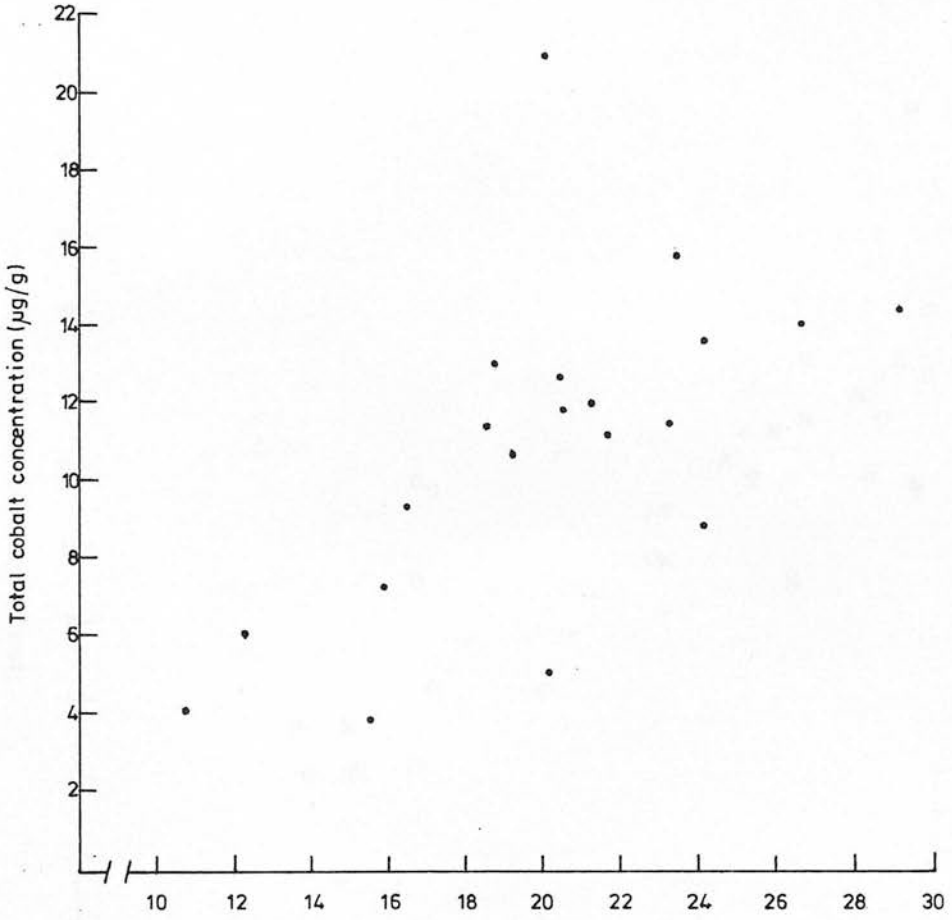


FIG. 4.1

Relationship between the total cobalt concentration and clay content in 20 soils from south-east Scotland.

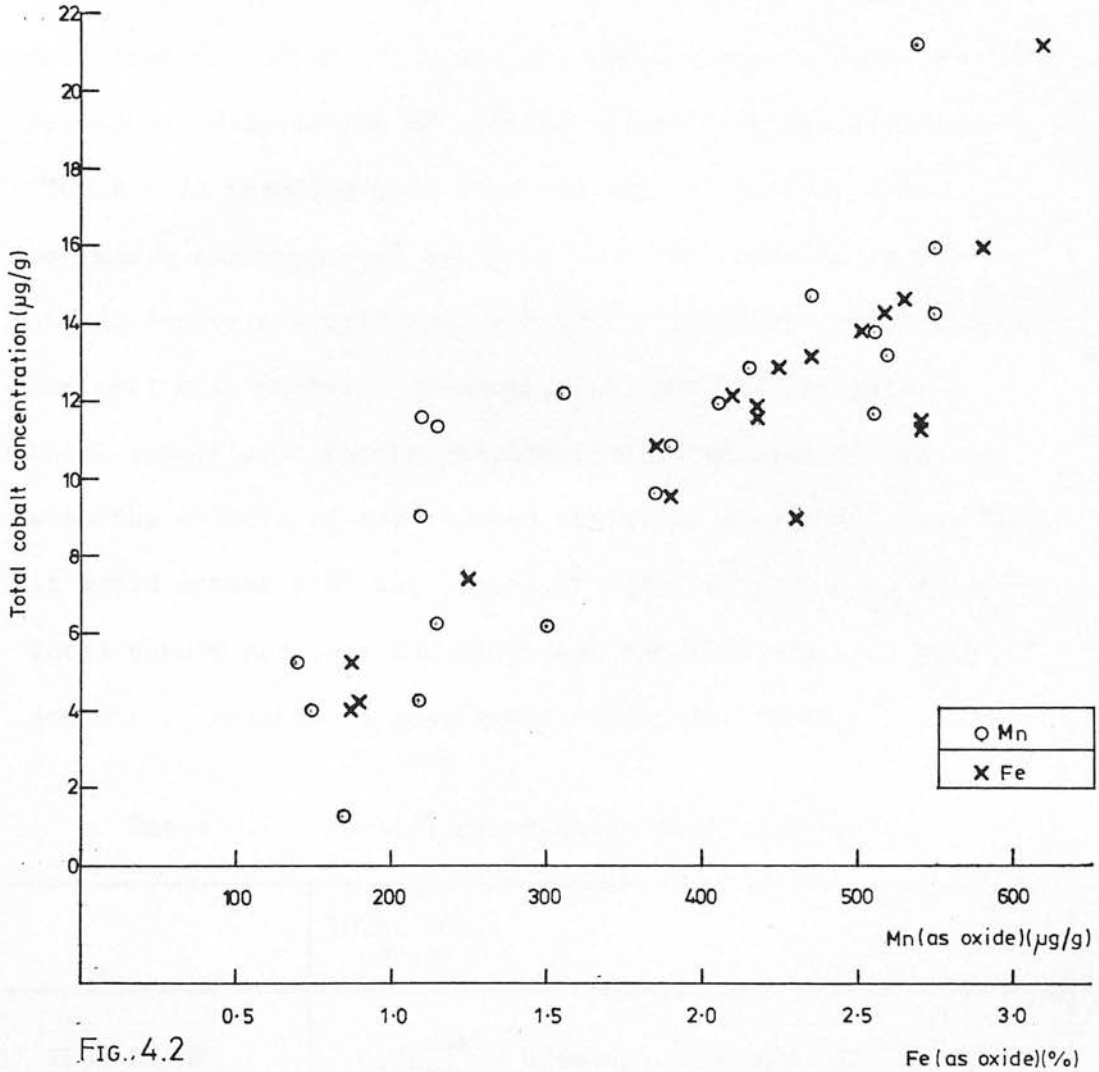


FIG. 4.2

Relationship between the total cobalt concentration and the manganese and iron oxide contents in 20 soils from south-east Scotland.

It has commonly been reported that soil cobalt content is directly related to the clay content eg Rana and Ouellette (1967); Andersson (1979).

However, for the 20 soils examined in this study, the soil clay content was significantly correlated to both soil iron ($r = 0.66$, $P < 0.01$) and manganese ($r = 0.56$, $P < 0.01$) contents. Calculation of partial correlation coefficients (Table 4.2) revealed that when the effects of iron and manganese contents were excluded from the correlation there was no longer a significant relationship between total cobalt and soil clay content. However, the correlations between total cobalt and iron or manganese remained significant even when the effects of the related variables were excluded. Thus it would appear that the important relationships are between total cobalt and iron and manganese contents and that cobalt content is related to clay content only indirectly.

Table 4.2 Partial correlation coefficients

	TOTAL SOIL COBALT	
SOIL IRON OXIDE	0.80^{xxx}	effects of Mn and clay excluded
SOIL MANGANESE OXIDE	0.65^{xx}	effects of Fe and clay excluded
SOIL CLAY	$-0.08^{n.s.}$	effects of Fe and Mn excluded

xxx $P < 0.001$
xx $P < 0.01$
n.s. not significant

It could be presumed, from the relationships shown above, that cobalt is bound by oxide material forming coatings on the clay minerals. Kubota (1965) observed that

podzols containing a textural B horizon had more dithionite-extractable cobalt than those without this feature. He suggested from this that cobalt was adsorbed by amorphous iron oxide coatings on the alumino-silicate clay particles

4.2.2 EXTRACTABLE SOIL COBALT

The concentrations of cobalt extracted from the 20 soils by 0.5 M acetic acid, 0.04 M di-sodium EDTA and 0.05 M $CaCl_2$ are presented in Table 4.3.

Table 4.3. Extractable soil cobalt

SOIL NO	Acetic acid [Co] (µg/g)	EDTA [Co] (µg/g)	$CaCl_2$ [Co] (µg/g)
1	0.09	0.13	0.001
2	0.54	1.14	0.002
3	0.31	1.71	0.151
4	0.28	1.73	0.144
5	0.62	2.70	0.164
6	0.42	1.58	0.051
7	0.36	0.51	0.008
8	0.43	1.01	0.485
9	0.28	0.90	0.113
10	0.30	1.61	0.072
11	0.60	1.21	0.017
12	0.24	1.40	0.005
13	0.18	0.36	0.003
14	0.43	1.03	0.021
15	0.66	2.01	0.079
16	0.29	0.59	0.364
17	0.45	2.08	0.071
18	0.81	1.31	0.274
19	0.45	2.63	0.176
20	0.26	0.64	0.191

In all the soils EDTA extracted more cobalt than acetic acid. In comparison, Mitchell (1972) reported that, in normal agricultural soils, 0.05 M EDTA extracted slightly less cobalt than 2.5% acetic acid whereas in soils with an

accumulation of organic matter in the surface horizon EDTA extracted 2 to 3 times the quantity of cobalt as acetic acid.

Seven of the soils in the present study had acetic acid-extractable cobalt levels below 0.3 μg/g and, from the observations of Mitchell (1963), it could be expected that these soils would support pasture herbage deficient in cobalt, in relation to ovine nutrition.

Although the EDTA and acetic acid-extractable cobalt concentrations were significantly correlated ($r = 0.51$, $P < 0.05$), there was no significant correlation between either of these values and calcium chloride-extractable cobalt. The calcium chloride-extractable cobalt levels were generally much lower than with the other two extractants although in a few soils the levels of calcium chloride and acetic acid-extractable cobalt were comparable.

The correlations between extractable cobalt concentrations and soil properties are shown in Table 4.4.

Table 4.4 Correlation coefficients between extractable soil Co and soil properties

	Total Co	$pH(H_2O)$	% clay	% org C	CEC	% Mn	% Fe
Acetic acid extble Co	0.58^{xx}	-0.07	0.31	-0.16	0.01	0.21	0.64^{xx}
EDTA extble Co	0.78^{xxx}	-0.18	0.49	-0.22	0.20	0.80^{xxx}	0.72^{xxx}
$CaCl_2$ extble Co	-0.19	-0.79^{xxx}	0.02	0.40	0.39	-0.24	0.01

xxx $P < 0.001$
xx $P < 0.01$

Both acetic acid and, to a greater extent, EDTA-extractable cobalt concentrations were correlated with the total soil cobalt contents. This is a reflection of their ability to extract cobalt from the soil oxides, which is indicated by the correlations with manganese and iron contents.

Since 0.5 M acetic acid has a pH of 2.5 a considerable proportion of the soil oxide fraction, especially manganese and aluminium oxides, would be dissolved during the extraction period. In Chapter 3 it was concluded that acetic acid mainly dissolved the more amorphous soil manganese oxides. From the small proportion of soil iron dissolved by acetic acid, it was concluded that it dissolved the amorphous forms of iron oxide.

EDTA is also likely to dissolve amorphous soil oxide material thus releasing any associated cobalt.

McLaren (1982), using 4 soils from the east of Scotland, observed that 0.04 M EDTA extracted, on average, 90 times more iron than 0.5 M acetic acid, but only 2 times as much manganese. The differences observed in the concentrations of cobalt extractable by acetic acid and EDTA in the present study (Table 4.3) thus appear to be attributable more to differences in manganese extractability than that of iron. McLaren (1982) observed that, whereas EDTA extracts only about 5 per cent of the soil oxide iron, it extracts 50-60 per cent of the oxide manganese. This suggests that a large proportion of the cobalt extracted by EDTA originates from the manganese oxides rather than the iron oxides.

EDTA is known to extract trace metals from soil organic matter (Borggaard, 1976), but there was no clear relationship between the total soil cobalt content or EDTA-extractable cobalt and soil organic carbon content. It is thus impossible to deduce the extent to which the soil organic matter fraction plays a role in binding EDTA-extractable cobalt.

Calcium chloride will extract soil cobalt which is in solution or easily exchangeable, the calcium ions displacing any cobalt which is held on the exchange sites of the clay and organic fractions of the soil. The concentrations of cobalt at these exchange sites are likely to be negligible so that calcium chloride will displace cobalt almost exclusively from soil solution.

Table 4.4 shows that the concentration of calcium chloride-extractable cobalt was negatively correlated with soil pH. This infers that the specific sorption reactions binding cobalt onto the solid phase of the soil are influenced by soil pH. This relationship is probably a result of the effect of pH on the equilibrium between cobalt sorbed on the surfaces of soil colloids and cobalt in soil solution. It is known that as pH decreases sorption decreases and soil solution cobalt concentration increases.

In contrast to EDTA and acetic acid soil cobalt extraction, there was no significant correlation between $CaCl_2$-extractable cobalt and total soil cobalt content. In the 20 soils the quantity of solid phase cobalt which is displaced into $CaCl_2$ solution appears to be unrelated to the total

concentration of cobalt in the solid phase.

4.2.3 ISOTOPICALLY EXCHANGEABLE SOIL COBALT

The quantity being measured by the isotope exchange technique is the amount of cobalt present in the solid phase of the soil which is able to exchange with cobalt present in solution. The concentrations of isotopically exchangeable cobalt (Co_{ie}) ranged from 0.04 to 0.74 μg/g with a mean value of 0.36 μg/g for the 20 soils (Table 4.5).

Table 4.5. Isotopically exchangeable soil cobalt

SOIL	Co_{ie} (μg/g)	SOIL	Co_{ie} (μg/g)
1	0.039	11	0.248
2	0.102	12	0.202
3	0.501	13	0.079
4	0.507	14	0.268
5	0.574	15	0.618
6	0.741	16	0.104
7	0.275	17	0.461
8	0.362	18	0.537
9	0.311	19	0.633
10	0.461	20	0.135

Although the Co_{ie} values were mostly similar to, or less than the acetic acid-extractable cobalt values, there were 7 soils in which the Co_{ie} values were markedly greater than the acetic acid-extractable values. It would be expected that acetic acid would extract cobalt present in soil solution and dissolve both isotopically exchangeable and some non-isotopically exchangeable cobalt. It is probable, therefore, that where Co_{ie} values are greater than the acetic acid extractable-cobalt values, a large

proportion of the isotopically exchangeable-cobalt is present on oxides which are non-soluble in acetic acid. The ratio of Co_{ie} : acetic acid-extractable cobalt concentration increases with soil manganese and iron contents, suggesting that the 'extra' isotopically exchangeable cobalt is present on the oxide fraction. There is little evidence, from the correlation coefficients in Table 4.6, that organic matter played an important role in holding isotopically exchangeable cobalt.

Table 4.6. Correlation coefficients of Co_{ie} with soil properties and extractable cobalt

	Total Co	pH(H_2O)	% clay	% org C	CEC	% Mn	% Fe	Acetic acid [Co]	EDTA [Co]	$CaCl_2$ [Co]
Co_{ie}	xxx 0.75	-0.23	x 0.55	-0.09	0.16	xx 0.66	xxx 0.72	x 0.51	xxx 0.81	0.15

xxx $P < 0.001$ xx $P < 0.01$ x $P < 0.02$

Although the EDTA-extractable cobalt values were greater than those of Co_{ie}, Table 4.6 shows that there was a more significant correlation between these two values than between Co_{ie} and acetic acid-extractable cobalt levels. This is possibly a result of EDTA being able to extract a greater proportion of the isotopically exchangeable cobalt than can acetic acid. An examination of partial correlation coefficients suggest that the dominant relationship in Table 4.6 was that between Co_{ie} and EDTA-extractable cobalt.

It should be noted that, although isotopically exchangeable cobalt can exchange with cobalt in solution, it would not exchange with other common cations in the soil, such as Ca^{2+} and Mg^{2+}. Isotopically exchangeable cobalt is most likely to be located on specific sorption sites associated with the soil colloidal fraction.

Gille and Graham (1971) measured isotopically exchangeable cobalt levels in the soil by measuring the distribution of added radioisotope between soil and sudangrass growing in the soil. They observed that a change in soil pH had no effect on the concentration of Co_{ie}. Variation in soil pH had no effect on Co_{ie} levels in the present experiment (Table 4.6).

Tiller et al. (1969) measured the concentration of isotopically exchangeable soil cobalt present in both the solid and solution phases. Their results showed a positive relationship between this measurement and soil pH. They also observed that isotopically exchangeable cobalt levels were significantly correlated with the sum of the quantities of soil cobalt extracted by ammonium acetate solution and quinol. It was suggested that these reagents extracted solution and easily exchangeable cobalt, along with that fraction sorbed on the easily reducible manganese. The association between Co_{ie} and the nitric/perchloric acid soluble iron and manganese in this present experiment has been noted.

The latter group of workers (Tiller et al. 1969) measured the total amounts of Co_{ie} present in the soil, that is, in both the solid and solution phases. A similar measurement was made for the soils in the present study and Table 4.7 presents the values for Co_{ie} (total) calculated from the equation:-

$$\left[Co_{ie}\ (total)\right] = \left[Co_{soln}\right] \times \frac{(^{58}Co\ original\ activity)}{(^{58}Co\ final\ activity)} \times 5$$

Table 4.7. Total isotopically exchangeable cobalt

SOIL	Co_{ie} (tot) ($\mu g/g$)
1	0.040
2	0.105
3	0.653
4	0.651
5	0.738
6	0.792
7	0.283
8	0.845
9	0.424
10	0.532
11	0.265
12	0.208
13	0.089
14	0.312
15	0.750
16	0.546
17	0.620
18	0.946
19	0.945
20	0.381

In most cases the values for Co_{ie} (total) were similar to those of Co_{ie} on the solid phase. There were a few soils in which the value for Co_{ie} (total) was significantly greater. In these soils the proportion of

isotopically-exchangeable cobalt in solution was high and therefore the 0.05 M calcium chloride extractable cobalt concentrations were also high (Table 4.3).

Table 4.8 presents the correlations between Co_{ie} (total) and other parameters of the 20 soils.

Table 4.8. Correlation coefficients of Co_{ie} (total) with soil properties and extractable Co

	Total Co	pH(H_2O)	% clay	% org C	CEC	% Mn	% Fe	Acetic acid /Co/	EDTA /Co/	$CaCl_2$ /Co/
Co_{ie} (tot)	0.48	xx -0.59	0.40	0.11	0.29	0.38	xx 0.57	x 0.53	xx 0.67	xx 0.63

xx $P < 0.01$ x $P < 0.02$

The total quantity of isotopically-exchangeable cobalt was indirectly related to soil pH and had a less significant relationship with soil manganese and iron contents than isotopically-exchangeable cobalt on the solid phase alone.

It was shown above that the concentration of specifically sorbed cobalt entering into $CaCl_2$ solution was pH dependent and it was suggested that this was a consequence of a change in the equilibrium between specifically sorbed and solution phase cobalt with variation in pH. It follows that the proportion of Co_{ie} (total) which remains specifically sorbed on the solid phase should also be pH dependent.

It is indeed found that the size of the ratio

$\frac{Co_{ie}\ (sorbed)}{Co_{ie}\ (total)}$ is pH dependent (corr, coeff 0.85; $P < 0.001$).

This ratio can be expressed more simply by the equation:-

$$1 - \frac{(^{58}Co \text{ final activity})}{(^{58}Co \text{ initial activity})}$$

It is therefore the distribution of the added radioisotope between the solid and solution phases which is highly pH dependent. The equilibrium reaction between the solution and specifically sorbed phases appears to have been less dependent of the concentration of cobalt present in the system than on soil pH.

4.3 Conclusions

The strong relationship in the 20 soils of total, acetic acid-extractable, EDTA-extractable and isotopically exchangeable cobalt levels with the iron and manganese oxide contents of the soils suggests that these materials play a large part in determining the behaviour of cobalt in the soil. It is probable that cobalt is also associated with the aluminium oxide fraction to some extent.

The results of the soil extraction with EDTA and acetic acid suggested that there were higher concentrations of cobalt associated with the manganese oxides than the iron oxides. However, as a consequence of their higher concentration in soil, the iron oxides will bind a significant proportion of soil cobalt.

In general 2-4 per cent of the total cobalt in soil was isotopically exchangeable. Thus most of the cobalt in soil would appear to be bound in non-isotopically exchangeable forms or occluded within the soil oxide fraction.

The proportion of total soil cobalt which could enter into calcium chloride solution ranged from 0.02 to 9.4 per cent, but was under 2 per cent for most soils. The percentage increased with decreasing soil pH as a result of the increased tendency of sorbed cobalt to enter into solution with decreasing soil pH.

In considering the abilities of the 3 soil extractants to extract different fractions of soil cobalt, it appears that both EDTA and acetic acid extract solid phase cobalt which could potentially enter into soil solution, the amount which does being dependent on solution pH.

Calcium chloride, in comparison, extracts cobalt which has entered into soil solution from the solid phase and also any cobalt present on the exchange complex.

The importance of organic matter in binding soil cobalt could not be ascertained from the results of the study. There was no significant correlation between total or extractable amounts with the percentage soil organic carbon content. However, it would be expected that EDTA would extract much of the cobalt associated with organic matter.

The properties of isotopically exchangeable cobalt differed according to the form being measured. For instance, the quantity of isotopically exchangeable cobalt measured in the solid plus solution phases was dependent on soil pH whereas that quantity measured in the solid phase alone was independent of soil pH. Therefore care should be taken in comparing results of isotopically exchangeable cobalt measurements in soils that the same quantity is being measured between studies. This is of particular importance where the proprtion of the isotopically exchangeable cobalt in soil solution is high.

CHAPTER 5.

THE EXTRACTABILITY OF SOIL COBALT WITH VARIATION IN SOIL MOISTURE CONTENT

The relationship between plant-availability of soil cobalt and the water content of soils has been evaluated by measuring the plant uptake of soil cobalt under different moisture conditions, or its extractability using different extraction solutions. The latter measurement has not always adequately reflected any change in the plant-availability of cobalt.

Hill et al. (1953), on measuring the cobalt content of alfalfa growing on soils of New Jersey, USA, reported that plants from poorly-drained soils were higher in cobalt than those from well-drained soils. This was in agreement with the results of Mitchell et al. (1957) which showed that vegetation growing on a poorly-drained soil had around 8 times the cobalt content of herbage growing in a well-drained soil in the same locality. Significant, but relatively smaller increases were found for nickel, but no increases were obtained in zinc and copper content. The 0.5 M acetic acid and 0.05 M EDTA extractable soil cobalt levels also increased under the poor drainage conditions.

From a pot experiment, Kubota et al. (1963) reported an increase in soil solution cobalt and the cobalt content of alsike clover, when soils were maintained at higher moisture levels. This increase was also observed with soil molybdenum, but not with soil copper.

Adams and Honeysett (1964) observed that soil waterlogging increased the native soil cobalt uptake by subterranean clover and ryegrass. This effect persisted even after soils, which had previously

been waterlogged, were air-dried. The waterlogging treatment also raised the copper contents of the plants, but to a much lesser extent than with cobalt. However, the change in plant cobalt content was not predicted by soil cobalt extraction with neutral 1N ammonium acetate or 0.1 N hydrochloric acid.

The following experiment, designed to monitor the effect of soil water content on the extractability of applied soil cobalt by 0.5 M acetic acid, was conducted on soils from the south-east of Scotland.

5.1 Experimental Method

5.1.1 SOILS

The 3 soils used in this experiment were also used in the cobalt extractability experiments described in Chapter 4. Their sampling from the field, and subsequent treatment, are described in section 4.1.1 of that chapter. The soils were chemically and physically analysed by the methods described in section 2.1. Acetic acid extractable soil cobalt was measured by the method described in section 2.2.1, except that the extraction was carried out at an ambient temperature of 20°C.

5.1.2 THE EXPERIMENT

Additions of cobalt sulphate, in 100 ml distilled water solution, were appled to 2.5 kg of soil at approximately 15 per cent moisture content. The soil and solution were mixed to incorporate the cobalt into the soil. The addition was designed to add 1.0 µg cobalt per gram of moist soil.

Approximately 200g samples of treated soil were placed in polystyrene pots and the following moisture treatments applied to them.

Constant low moisture: Soil moisture content was maintained at 15% by the addition of distilled water. The pots were unsealed to maintain aerobic soil conditions. The soil moisture content was measured, at intervals of about 3 days, by weighing the pots and soil. The soil in each pot was also thoroughly agitated at regular intervals to ensure aerobic conditions throughout the pot.

Periodical waterlogging: Soil moisture content was increased to 45% by the addition of distilled water. The soil was then allowed to dry to around 15% moisture before rewetting to 45%. This was repeated for the duration of the experiment. The pots were sealed with perforated lids in order to prolong the period required for drying. The soil in the pot was thoroughly mixed at regular intervals.

Constant waterlogging: Soil moisture content was increased to 45% by the addition of distilled water and maintained at a level above 30% for the duration of the experiment. The pots were sealed to ensure the maintenance of conditions in the soil.

In all treatments, the soils were kept at an ambient temperature of 20°C in an incubator. There were 3 replicates for each soil and treatment; a total of 27 pots.

Samples from the pots, weighing between 7g and 8g, were extracted, in a moist state, with 0.5 M acetic acid solution by the method referred to in section 5.1.1.

5.2 Results and Discussion

The 3 soils used were those numbered 7, 9 and 17 of the soils used in the experiment in Chapter 4. The results of their analyses are presented in Table 5.1.

Table 5.1. Analyses of moisture experiment soils

SOIL	pH_{H_2O}	% clay	% organic carbon	CEC (m.equiv.) per 100g	nitric/perchloric acid		
					Mn(µg/g)	Fe(%)	Co(µg/g)
7	7.1	15.9	1.9	13.8	170	1.24	7.31
9	5.9	16.5	3.3	23.9	370	1.91	9.42
17	6.4	23.4	2.7	23.8	550	2.93	15.80

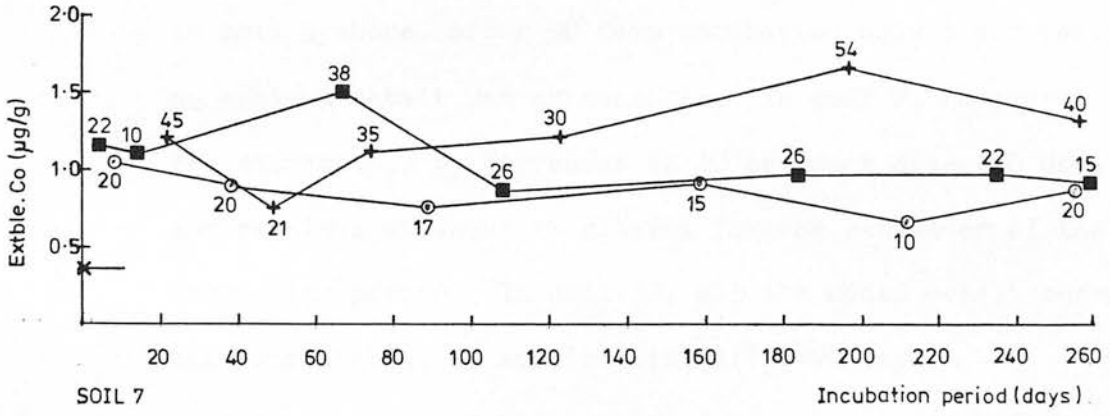
5.2.1 ACETIC ACID-EXTRACTABLE COBALT

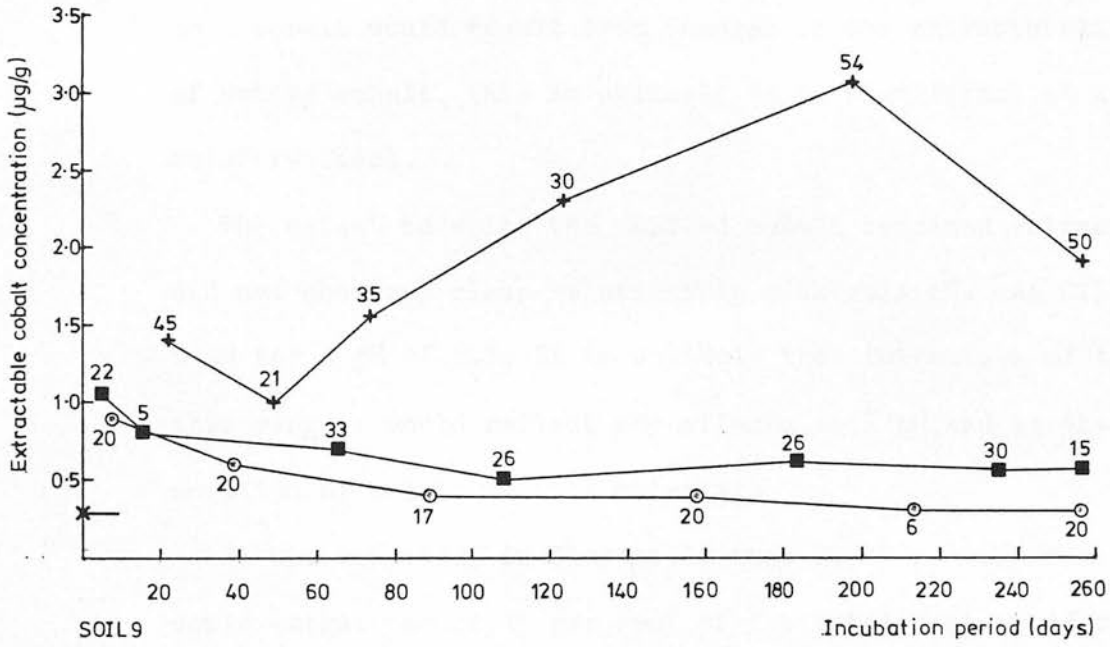
The acetic acid-extractable soil cobalt concentrations, for the 3 soils, expressed on an air-dry weight basis, are presented in Fig . 5.1.

The soil moisture contents at the point of sampling and the acetic acid-extractable cobalt value for untreated air-dry soils measured before the experiment are also given.

Low moisture treatment

In soils 7 and 9, approximately 50 per cent of the added cobalt was still extractable 10 days after its application, but in soil 17, the equivalent proportion was only 8 per cent. In all three soils there was a decrease, to a varying degree, in the extractable cobalt levels during the subsequent incubation period. This decline in extractability remained most evident





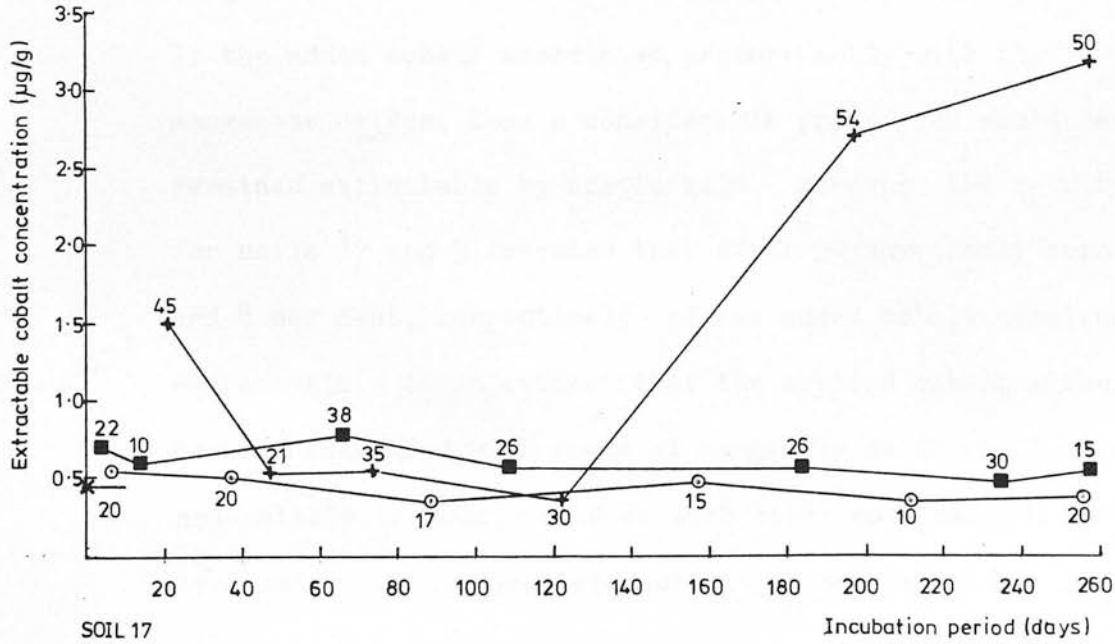


FIG.5.1 Concentration of cobalt extractable by 0·5M acetic acid in soil under different soil moisture regimes. ○ – Low moisture ■ – Periodical waterlogging + – Constant waterlogging ✕ – Extractable native Co. Figures denote % soil moisture.

in soil 9 where, after 90 days incubation only 8 per cent of the applied cobalt was extractable. In soil 7, however, the extractability decreased to 30 per cent after 90 days and remained at about this level for the remainder of the incubation period. In soil 17, all the added cobalt became non-extractable, by acetic acid, after 70 days.

Although some of the variation in the extractability of soil cobalt would result from changes in the extractability of native cobalt, this is unlikely to be significant at a low moisture level.

The extent to which the applied cobalt remained extractable did not show any clear relationship with soil pH. As 0.5 M acetic acid has a pH of 2.5, it is unlikely that extraction of the soil with this reagent would reflect any effects soil pH had on the sorption of cobalt to soil material.

It was reported, in Chapter 2, that 0.5 M acetic acid could extract about 15 per cent of the total content of soil manganese as compared to about 0.1 per cent of the total iron. If the added cobalt associated predominantly with the manganese oxides, then a considerable proportion would have remained extractable by acetic acid. However, the results for soils 17 and 9 revealed that after 90 days, only zero and 8 per cent, respectively, of the added cobalt remained extractable. It is evident that the applied cobalt either became associated with forms of manganese oxide which were non-soluble in acetic acid or with other soil oxides, such as iron oxide, which were less soluble in acetic acid.

During the low moisture soil incubation aerobic conditions would cause further oxidation of metal oxide material, resulting in the occlusion of associated cobalt. Cobalt could also move into the oxide structure by replacement of the major metal ion. These factors would cause a decrease in the extractability of soil cobalt.

The extractability of cobalt in soil 7 remained much higher than in the other two soils. This may have been a result of the lower iron and manganese oxide contents resulting in a relatively higher cobalt concentration at the oxide surface. It is probable that the greater the concentration of cobalt sorbed, the less energy with which it is held.

No relationship between the extractability of cobalt and the amount of organic matter present in the soil could be observed from the results.

Constant waterlogging treatment.

Soils 9 and 17 show evidence that soil waterlogging caused mobilisation of native cobalt (Figs. 5.2, 5.3). Both soils showed a maximum increase of about 2.6 µg/g in extractable cobalt levels whereas only about 1.2 µg cobalt was added per gram air-dry soil. The levels of extractable cobalt in these two soils were almost always above the levels in the low moisture treatment, even although the moisture content decreased to below 40 per cent during the first half of the incubation period.

Ng and Bloomfield (1962) reported a $2\frac{1}{2}$ times increase in the amount of native cobalt which was extractable by 2.5% acetic acid in a top soil after 39 days of anaerobic incubation.

A similar proportional increase in acetic acid-extractable cobalt was obtained, by Mitchell et al. (1957), in a comparison of soil under well drained and poorly drained conditions.

The increase in cobalt extractable by 0.5 M acetic acid would be a consequence of the reduction of the soil oxides under the anaerobic conditions. This causes an increase in the solubility of the oxides in acetic acid, resulting in the native and applied cobalt associated with these oxides being released into acetic acid solution.

In a soil incubation experiment, Ng and Bloomfield (1962) observed that the amount of iron extracted by 1N ammonium acetate, at pH 3.0, increased markedly for up to 20 days of soil incubation. However, the amount of manganese extracted by the same reagent declined slightly under anaerobic incubation. Cobalt behaved in a similar manner to the soil iron.

Cobalt added to soil 7 exhibited different behaviour to that in the other two soils (Fig. 5.1). The maximum increase in extractable cobalt over the incubation period was only 1.3 μg/g. Throughout the major part of the incubation period the waterlogging treatment caused an increase ranging from 0.3 μg/g to 0.8 μg/g in the extractable cobalt content above that in the low moisture treatment. The corresponding increase ranged from 0.5 μg/g to 2.5 μg/g, in soil 9, and zero to 2.8 μg/g in soil 17. Thus, in soil 7 the extractable cobalt level remained comparatively constant indicating that in this

soil, anaerobic conditions had little effect on the extractability of cobalt.

It is of note that soil 7 had a lower organic carbon content than the other two soils (Table 5.1) so it is likely that reducing conditions did not occur to the same extent as in the other soils.

Periodical waterlogging treatment.

In all 3 soils, intermittent waterlogging caused only a small increase in the extractability of soil cobalt by acetic acid. It should be noted that the measurements were generally made when the soil moisture content was below 30 per cent. This indicates that the effects of waterlogging quickly decreased when aerobic conditions were re-established in the soils. Adams and Honeysett (1964) concluded, from the uptake of cobalt by ryegrass growing on waterlogged soil, that much of the cobalt released by waterlogging was ephemeral and able to be absorbed only by rapidly growing plants.

Ng and Bloomfield (1962) reported a decrease in the extractability of soil cobalt by 2.5% acetic acid after a waterlogged soil was allowed to re-oxidise. This happened within a period of 4 days aeration. The concentration of iron extractable by 1N ammonium acetate (pH 3.0) also decreased with the aeration of a previously waterlogged soil. However, the concentration of manganese extracted by this reagent increased with the period of aeration.

From Figs. 5.1 to 5.3 it is apparent that, even with intermittent soil waterlogging, there was significant fixation of the added cobalt during the incubation period in soils 9 and 17. However, in soil 7 a considerable fraction of the added cobalt remained extractable by acetic acid.

The fixation of cobalt over the incubation period was probably caused by the occlusion of cobalt with soil oxides. The fixation of the added cobalt in soils 9 and 17 suggests that the occlusion took place with oxides of iron or stable manganese oxides which are relatively resistant to solubilisation by acetic acid.

The different behaviour shown by cobalt in soil 7 was probably for the same reasons as in the 'constant waterlogging' treatment.

The decrease in extractability of cobalt over the incubation period was probably a consequence of a reduction in the decrease of redox potential with each successive waterlogging. This phenomenon was reported by Patrick and Wyatt (1964). In this way, the soil oxides would remain more stable during the incubation period than in a constantly waterlogged soil. The cobalt associated with these oxides would become less extractable with time as a result of occlusion or the movement of cobalt into the oxide structure.

5.3 Conclusions

Of the 3 soils studied, the acetic acid extractability of added cobalt, under low moisture conditions, remained highest in soil 7. This was thought to be attributable to the low iron and manganese oxide contents in this soil, causing the supplementary cobalt to be specifically sorbed at lower energy. However, an increase in the reducing conditions of soil 7 had comparatively little effect on the concentration of cobalt extractable by acetic acid. This may have been a result of a number of factors. Firstly, because of the high soil pH the soil oxides would be less susceptible to reduction and so a smaller amount of associated cobalt would be released into acetic acid solution. Secondly, the proportion of the added cobalt which became associated with the soil oxides would be smaller than in the other two soils studied, as a result of the lower manganese and iron oxide contents. Thus a greater proportion of the added cobalt could be sorbed by the clay mineral fraction and the extractability of this cobalt would be little affected by anaerobic soil conditions. Lastly, the low organic matter content of soil 7 would cause the reducing conditions to be less severe than in the other two soils.

It is apparent that, in a field situation, pasture herbage on this soil would be low in cobalt content throughout the growing season. Even fluctuations in the soil moisture content would not affect the plant-availability of soil cobalt.

In soils 9 and 17, it was observed that waterlogging over a period of 8 months caused a large increase in the extractability of cobalt by acetic acid. These conditions are unlikely to be

encountered in agriculture in temperate climates, but, on poorly drained soils, there may be intermittent waterlogging. The effects of this condition on the extractable cobalt levels in soils 9 and 17 were short lived, however, and it was evident that cobalt became occluded by the soil oxides once aerobic conditions returned. Therefore the period of plant growth at which any increase in soil moisture took place would be important in influencing the plant uptake of cobalt. Only actively growing plants could take advantage of any cobalt released into soil solution.

Despite the periodical waterlogging, in soils 9 and 17, there was an increase in the fixation of cobalt over the incubation period so that its extractability in acetic acid decreased. Thus, in the field situation, where there are fluctuations in the soil moisture content, it would be expected that the extractability of applied cobalt would decrease. The plant-availability of applied cobalt would also probably be diminished over time.

The major cause of cobalt fixation in the periodically waterlogged soils would be the movement of cobalt into oxides of a more crystalline nature resulting in the cobalt being less extractable by acetic acid.

The results also showed that, unless there are large differences in the moisture status of soils, variability in the level of cobalt which is potentially plant available (as measured by acetic acid extraction) is likely to be governed by the chemistry of the soils rather than variability in soil moisture.

CHAPTER 6.

SORPTION OF COBALT BY SOILS AND SOIL COMPONENTS

Laboratory experiments to measure the extent of the specific sorption of cobalt by soils have been carried out in an attempt to determine which soil components are of importance in this process. Manganese oxides (Tiller *et al.* 1969) and iron oxides (Abd-Elfattah and Wada, 1981) have both been implicated as being of importance.

The mechanism of cobalt sorption by clay minerals has been the subject of investigations by a number of workers (Hodgson, 1960; Hodgson, Geering and Fellows, 1964; Hodgson, Tiller and Fellows, 1964; McKenzie, 1963; Spencer and Gieseking, 1954; Egozy, 1980 and Peigneur *et al.* 1975). Most studies have shown that on clay minerals, there is more than one type of specific bonding reaction for cobalt.

The ability of manganese oxide to sorb cobalt has been widely reported. McKenzie (1967) observed that cobalt is held on soil manganese oxide minerals with greater bonding energy than copper or nickel. Loganathan *et al.* (1977) observed that cobalt is held with greater energy than zinc on δ-MnO_2.

Studies of cobalt sorption by iron oxides and hydroxides have been carried out by Forbes *et al.* (1976), Benjamin and Leckie (1981) and Polgar (1975). The iron oxides displayed an ability to specifically sorb cobalt with relatively high energy.

The sorption of cobalt onto oxides of aluminium, titanium and zirconium has been investigated by Tewari *et al.* (1972), and Tewari

and Lee (1975), and on silicon and titanium oxides by James and Healy (1972a).

Sorption of cobalt onto soil organic matter has been restricted mainly to studies on humic and fulvic acids. Studies on humic acid have been conducted by Dunigan and Francis (1972), Kerndorff and Schnitzer (1980) and Khan (1969), and a fulvic acid by MacCarthy and O'Cinneide (1974), Schnitzer and Skinner (1967) and Stevenson and Ardakani (1972). These studies showed that the energy with which cobalt is bound by organic matter is lower than with other 1st series transition metals such as copper, iron, nickel and zinc.

Hodgson et al. (1965) investigated the concentrations of cobalt, copper and zinc likely to be organically complexed in soil solution. The concentrations of organically complexed cobalt and zinc were much lower than that of copper.

The aims of the present experiment were to compare the sorption of cobalt by soils and different soil constituents, from solutions in which the concentrations of cobalt were similar to those likely to be encountered in soil. The effects of pH and ionic strength of the solution on cobalt sorption by the soil materials were investigated, along with the isotopic exchangeability of sorbed cobalt.

6.1 Experimental Method

6.1.1 MATERIALS USED IN SORPTION EXPERIMENTS

Soils: Cobalt sorption experiments were carried out on the soils used in the cobalt extractability experiment described in Chapter 4.

Montmorillonite: No. 27 standard A.P.I. Project 49 from Belle Fourche, South Dakota.

Kaolinite: from English China Clays, Cornwall.

Illite: No. 36 standard A.P.I. Project 49 from Morris, Indiana.

All samples used of each of the 3 clay minerals had particle size < 2 μm. The clay minerals were saturated with calcium using 0.05 M $CaCl_2$ and then washed with deionised water.

Soil oxide material: ferro-manganese concretions were obtained from a soil of the Fladbury Series in South Nottinghamshire (Crawford, 1969). This material contained 13.2% iron and 5.8% manganese. It was finely ground in an agate ball-mill before use.

Birnessite (pure and impure): samples of pure birnessite and birnessite containing clay mineral impurity were supplied by the Macaulay Institute for Soil Science, Craigiebuckler, Aberdeenshire. The pure birnessite contained 1.9% iron and 3% manganese. The samples were ground in an agate ball-mill before use.

Minerals of Geological Origin: Samples of manganite, pyrolusite, goethite and haematite were obtained from the Geology Department of the University of Edinburgh. The samples were finely ground in an agate ball-mill before use.

Humic acid and Fulvic acid: prepared from basin peat in the Bush Estate, Midlothian by extraction with 0.5 M sodium hydroxide. The fulvic acid was obtained by adjusting the pH of the extract to about 1.0 and centrifuging. The resulting supernatant contained the fulvic acid fraction.

The centrifugate was dissolved in distilled water and adjusted to pH 7.0. This solution was then centrifuged and the pH of the resulting supernatant adjusted to about 1.0. This was, in turn, centrifuged leaving the humic acid fraction in the centrifugate.

Both the humic acid and fulvic acid were dialysed to remove unwanted ions and then saturated with calcium by successive treatments with 0.5 M $CaCl_2$ and 0.25 M $CaCl_2$. The two fractions were then washed with deionised water.

6.1.2 SORPTION EXPERIMENTS

Sorption of cobalt by soil constituents and geological materials

Samples of sorbent material were equilibrated in polypropylene tubes with solutions containing known amounts of cobalt labelled with cobalt-58 (0.1-1.0 μCi/ml). Equilibration was carried out at 20°C on a rotary shaker.

After the desired equilbration period had elapsed, the tubes were centrifuged for one minute at 3,000 rpm and the clear solution shaken onto the top of the tube in order to dislodge any particulate matter between the stopper and wall of the tube (Hodgson, 1963).

The tubes were then recentrifuged at 6,000 rpm for 15 minutes and aliquot samples of the supernatant solution were taken by Gilson pipette and transferred to glass scintillation counting phials. The activities of the samples were then measured using a Panax "Reigate Series", well-type scintillation counter equipped with a NaI crystal containing Tl impurity.

The activities of the samples were compared with those of blank samples, prepared in a similar fashion, without sorbent material. The difference in activity between the sample and blank resulted from the sorption of radioactive cobalt-58 by the sorbent material.

It was assumed that the cobalt-58 entered into the same sorption and desorption reactions as the non-radioactive cobalt-59 so that at equilibrium (between sorbed cobalt and solution cobalt) the proportions of cobalt-58 and cobalt-59 remaining in solution were identical. From the initial concentration of non-radioactive cobalt and the proportion of radioactive cobalt sorbed, the amount of non-radioactive cobalt sorbed could be calculated.

(a) THE EFFECT OF TIME ON COBALT SORPTION

To 0.4g sorbent material in a 50 ml tube, 40 ml cobalt solution containing radioactive cobalt-58 was added. The solutions contained 0.05 molar $CaCl_2$ and were adjusted to pH 6.0 using $Ca(OH)_2$ solution. Volumes of 0.1 M HCl were added to the

montmorillonite systems to maintain the solution pH at 6.0 throughout the sorption period. The initial solution cobalt concentrations were: soil oxide, 2.0 ppm Co; humic acid, 1.6 ppm Co; and montmorillonite, 0.4 ppm Co.

The tubes were shaken for a total of 95 hours and at various intervals were centrifuged and 0.1 ml samples of the supernatant solution taken for scintillation counting.

The results (Fig 6.1) showed that equilibrium was attained in 20 hours in the soil oxide and humate systems whereas with montmorillonite sorption increased rapidly up to a period of 40 hours after which there was a smaller but steady increase in sorption.

Since this secondary sorption represented only a small proportion of the total sorption onto the montmorillonite, 48 hours was adjudged to be a satisfactory equilibration period for all 3 materials.

(b) THE EFFECT OF SOLUTION IONIC STRENGTH ON COBALT SORPTION

Samples of sorbent material weighing 0.1g were shaken for 48 hours with 10 ml volumes of cobalt solution in 15 ml centrifuge tubes. The background $CaCl_2$ concentrations were varied from 0.0005 M to 0.5 M, and adjusted to pH 6.0 using small volumes of 0.1 M HCl or saturated $Ca(OH)_2$ solution. Additional volumes of 0.1 M HCl were added to the montmorillonite

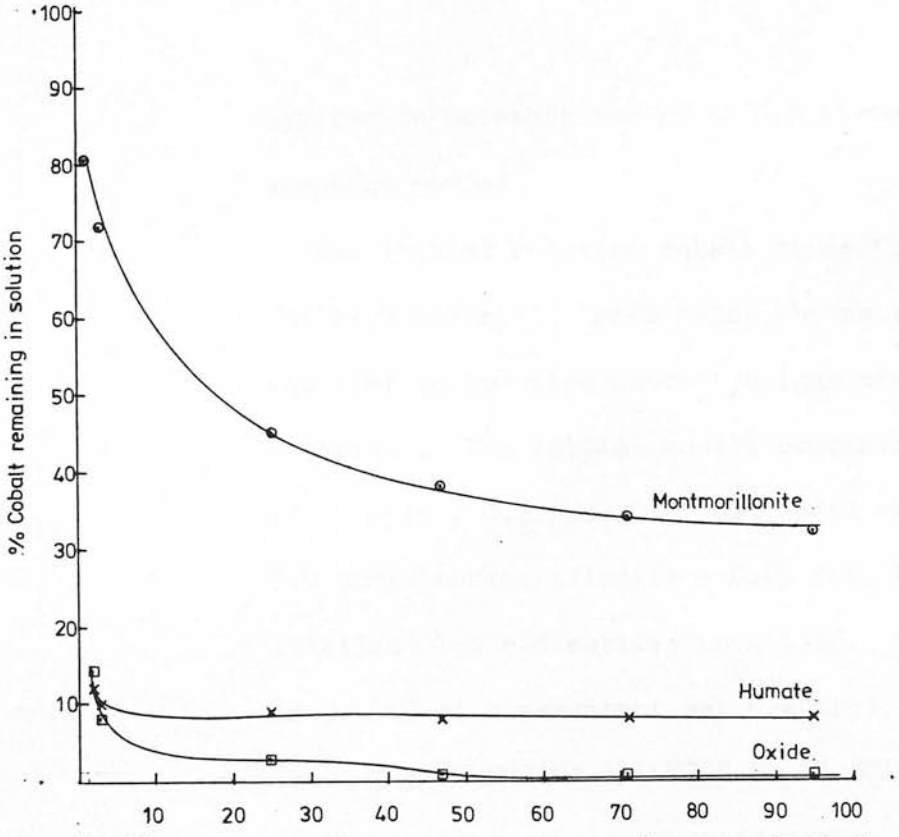


FIG. 6.1

Effect of time on the sorption of cobalt by soil constituents.

Initial soln. Co concn.- Mont.: 0·4 µg/ml; Humate: 1·6 µg/ml; Oxide: 2·0 µg/ml

Background electrolyte - 0·05M $CaCl_2$

Final soln. pH - Mont.: 5·9; Humate: 5·6; Oxide: 6·4

systems to maintain the pH at 6.0 throughout the sorption period.

Two initial solution cobalt concentrations were used for each material, these being chosen to give similar equilibrium solution concentrations among the materials. The initial cobalt concentrations were: humic acid - 0.2 ppm, 0.8 ppm; soil oxides - 2.0 ppm. 8.0 ppm; montmorillonite - 0.05 ppm, 0.2 ppm, all labelled with radioactive cobalt-58. The activity in 5.0 ml of supernatant was measured.

(c) THE EFFECT OF SOLUTION pH ON COBALT SORPTION

The initial cobalt concentrations, labelled with cobalt-58, sample weights and solution volumes were the same as those used in the 'ionic strength' experiment. All solutions were 0.01 molar with respect to $CaCl_2$ and the solution pH was varied using 0.1 M HCl or saturated $Ca(OH)_2$ solution.

(d) COBALT SORPTION WITH MAGNESIUM AS COMPETING ION

The background solutions, in this experiment, contained either:

1. 0.02 M $CaCl_2$ at pH 6.0; or
2. 0.01 M $CaCl_2$ plus 0.01 M $MgCl_2$ at pH 6.0.

The initial solution cobalt concentrations, containing Co-58 were:-

montmorillonite - 0.02 ppm; humic acid - 0.16 ppm; impure birnessite - 0.16 ppm.

The sorption on montmorillonite was repeated using solutions 1. and 2. in ethanol in order to eliminate hydrolysis of solution cobalt.

(e) COBALT SORPTION ISOTHERMS

The sorbing solutions, in this study, were 0.01 M in $CaCl_2$ and at pH 6.0. The initial solution concentrations of cobalt, labelled with cobalt-58, were varied.

With some of the materials, the desorption of sorbed cobalt was examined by decanting the residual supernatant after the sampling for activity measurement. A 10.0 ml volume of 0.01 M $CaCl_2$ was then pipetted into each tube and, after dislodging the solid centrifugate by mechanical force, the tubes were shaken for a further 24 hours. They were then centrifuged as before and 5.0 ml samples of supernatant taken for activity measurement. The tubes plus the centrifugate and residual solution were weighed, after decanting, in order to measure the volume of solution remaining in the solid pad. The activity attributable to this residual solution was taken into account in measuring the amount of cobalt desorbed. The desorption process was repeated sequentially.

Sorption on intact soils.

COBALT SORPTION ISOTHERMS

To 4.0 g of finely ground soil samples, in 50 ml polypropylene centrifuge tubes, 20 ml volumes of 0.01 M $CaCl_2$ solution (pH 6.0), containing varying concentrations of cobalt, were added. The initial cobalt concentration was varied from zero to 0.20 ppm.

The soil and solution cobalt were allowed to equilibrate for 72 hours by shaking the centrifuge tubes in a rotary shaker. The tubes were then centrifuged at 6,000 rpm for 10 minutes before 10 ml samples of supernatant were taken for cobalt analysis by flameless atomic absorption spectrophotometry. The method of analysis is described in section 2.4.2.

The pH of the supernatant was measured using a Pye Unicam Model 290 Mk 2 pH meter equipped with a combined glass/calomel electrode.

The quantity of cobalt sorbed was calculated as the difference between the initial and final concentration of cobalt in solution. In some cases a significant proportion of the solution cobalt was derived from native cobalt desorbed from the soil.

6.1.3 ISOTOPIC EXCHANGEABILITY EXPERIMENTS

The effect of time on the isotopic exchangeability of cobalt sorbed on soil constituents

Samples of material (0.4g) were equilibrated in 50 ml polypropylene centrifuge tubes with 40 ml volumes of solution containing known concentrations of cobalt. The initial solution cobalt concentrations were montmorillonite - 0.1 ppm; humic acid - 0.2 ppm; soil oxide - 8.0 ppm. The pH of all the solutions was adjusted to 6.0 and the montmorillonite samples were maintained at this value during equilibration by the addition of small volumes of 0.1 M HCl. To reduce the possibility of the oxidation of the humic acid during equilibration, air was expelled from the tubes with oxygen-free nitrogen gas before sealing.

Equilibration was carried out at 20°C on a rotary shaker for a total of 54 days. At various times within this period duplicate tubes for each material were removed from the shaker and centrifuged at 6,000 rpm for 10 minutes. A small volume (0.1 ml) of carrier-free cobalt-58 in calcium chloride solution was then added carefully to the supernatant solutions. After gentle manual shaking, to allow mixing of the radioactive cobalt throughout the solution, the centrifuged materials were re-dispersed by strong agitation of the tubes and then equilibrated for a further 48 hours on the rotary shaker.

The samples were then re-centrifuged and 5 ml samples of supernatant solution were then taken for measurement of cobalt-58 activity. Samples of supernatant solution (10 ml) were also taken for cobalt analysis by flameless atomic absorption spectrophotometry (see section 2.4.2).

6.2 Results

The data for the results of the sorption experiments are included in the appendices.

6.2.1 EFFECT OF SOLUTION IONIC STRENGTH ON COBALT SORPTION

Figures 6.2 and 6.3 show the effect of change in the calcium chloride solution concentration on the quantity of cobalt sorbed by humic acid, montmorillonite and soil oxides. It should be noted that the calcium ion concentration is in large excess relative to that of cobalt, and that if cobalt is held on the solid phase solely by cation exchange processes then virtually no sorption would have been observed. Cobalt

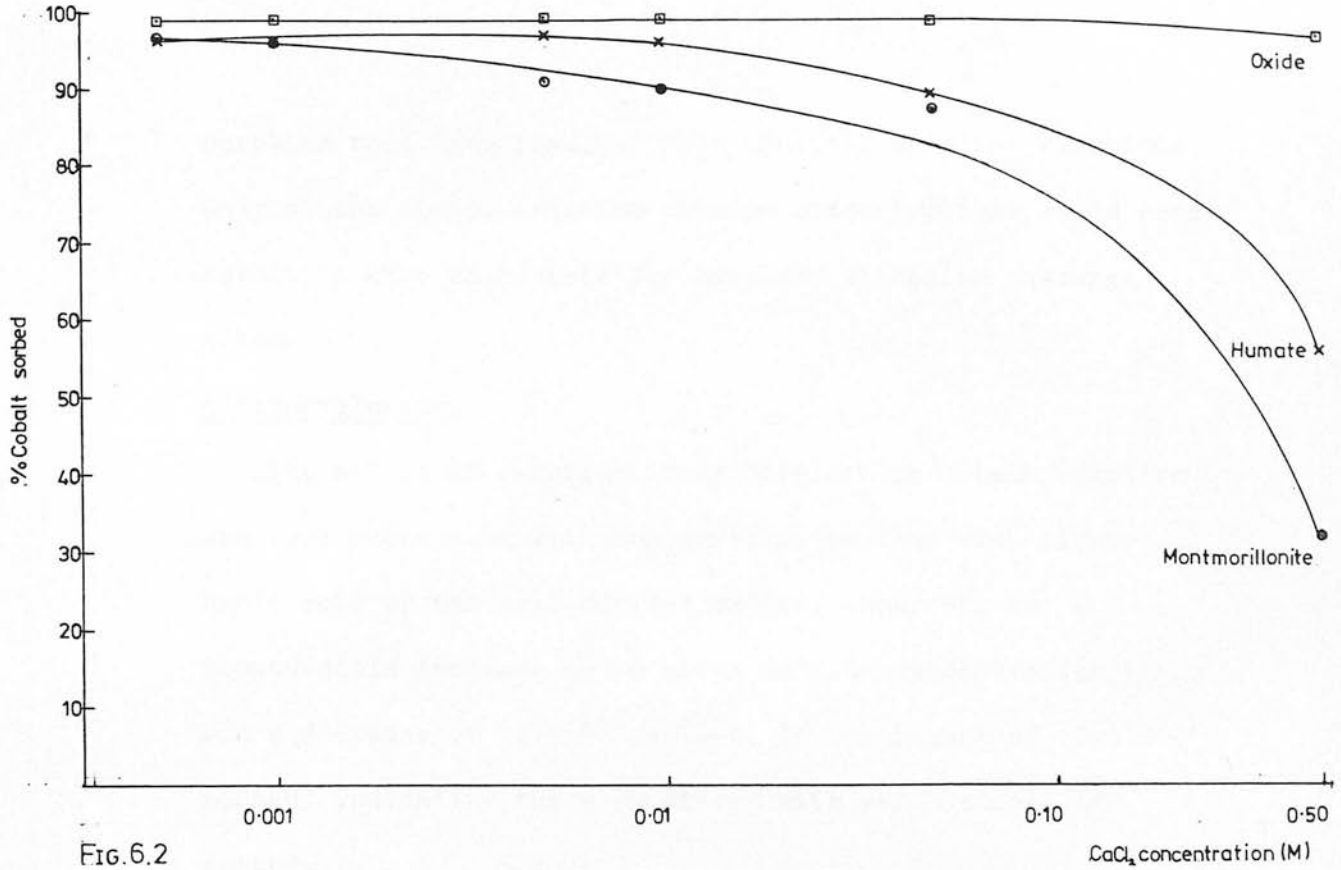


FIG. 6.2

Effect of solution ionic strength on cobalt sorption by soil constituents.

Initial soln. Co concn.- Mont.: 0·05 µg/ml ; Humate: 0·2 µg/ml ; Oxide: 2·0 µg/ml

Final soln. pH - 5·9 - 6·1

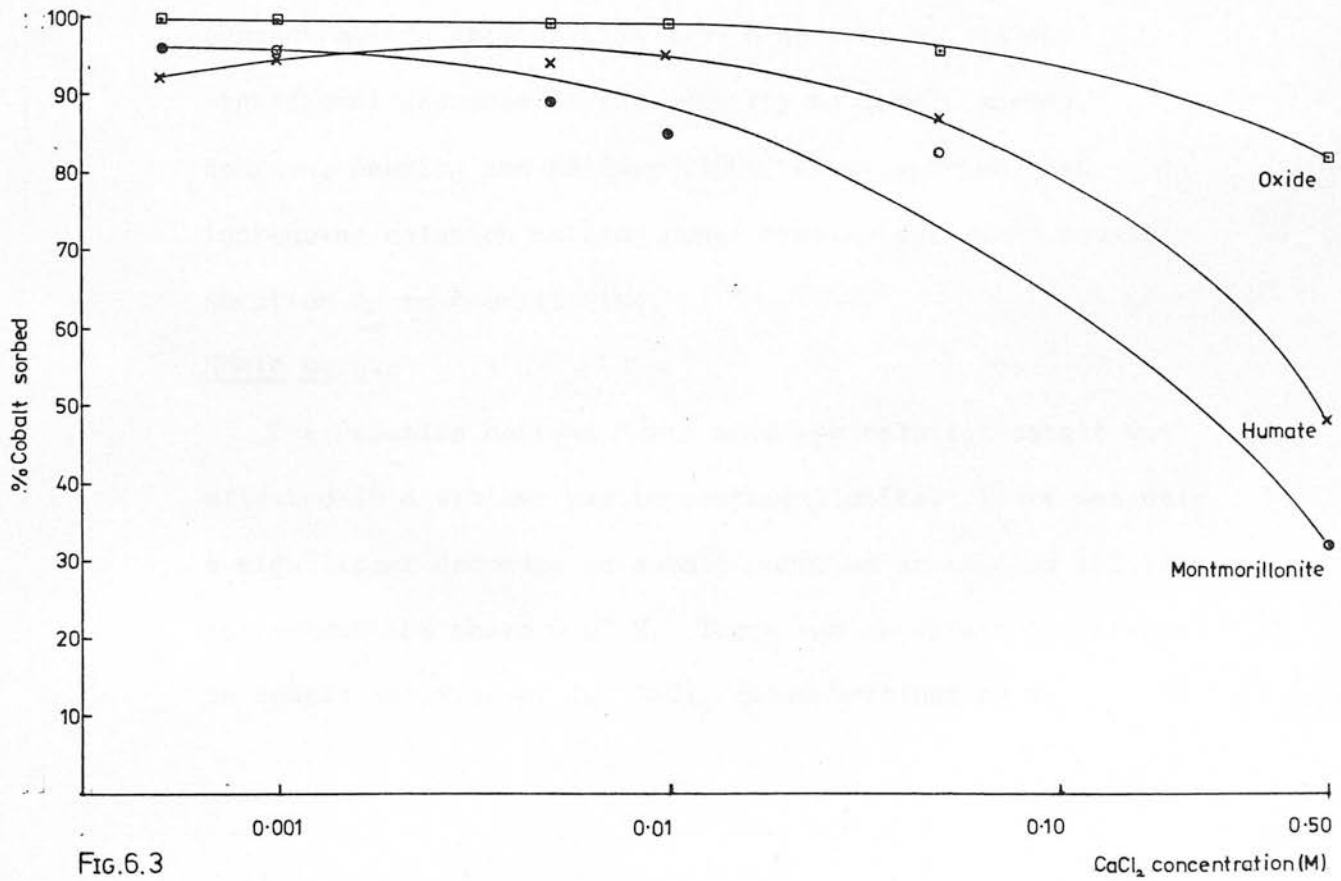


FIG. 6.3

Effect of solution ionic strength on cobalt sorption by soil constituents.

Initial soln. Co concn.- Mont.: 0·2 µg/ml ; Humate: 0·8 µg/ml ; Oxide: 8·0 µg/ml

Final soln. pH - 5·9 - 6·1

sorption must have resulted from specific sorption reactions. Only at the lowest solution calcium concentrations would some cobalt be able to compete for sorption at cation exchange sites.

Montmorillonite.

The effect of solution ionic strength on cobalt sorption was more pronounced with montmorillonite than with either humic acid or the soil-derived oxides. However, for a thousandfold increase in solution calcium concentration there was a decrease of only 67 per cent in the amount of cobalt sorbed, indicating the high energy with which cobalt was sorbed.

It is notable that, at normal solution calcium concentrations of around 0.01 M, at least 90 per cent of the cobalt was in the sorbed state. It was only at solution calcium concentrations greater than 0.01 M that there was any significant decrease in the quantity of cobalt sorbed. Hodgson, Geering and Fellows (1964) also reported that increasing solution calcium concentration decreased cobalt sorption by montmorillonite.

Humic acid.

The reaction between humic acid and solution cobalt was affected in a similar way to montmorillonite. There was only a significant decrease in cobalt sorption at calcium solution concentrations above 0.01 M. There was an apparent decrease in cobalt sorption at low $CaCl_2$ concentrations as a

consequence of humic acid dispersion into solution. This would also carry sorbed cobalt into solution in a colloidal state. Although not present in the solution as the cobaltous ion, it would be detected in analysis by solution radioactivity measurement.

Schnitzer and Hansen (1970), in studying the stability constants of transition metal-fulvic acid complexes, have observed a decrease in stability with increasing ionic strength.

Soil oxides.

The very high energy with which the soil concretion oxide material sorbed cobalt was evident from the small effect increases in ionic strength had on cobalt sorption. At a solution concentration of 0.01 M $CaCl_2$, there was almost complete sorption of solution cobalt, and even at $CaCl_2$ concentrations of 0.5 M, over 80 per cent of the cobalt in the system remained sorbed.

6.2.2 EFFECT OF SOLUTION pH ON COBALT SORPTION

Sorption experiments were carried out at a $CaCl_2$ concentration of 0.01 M so that no non-specific cobalt sorption reactions ie cation exchange; could take place. Figures 6.4 and 6.5 show that the specific sorption of cobalt by the 3 soil components was reduced with decreasing solution pH.

Montmorillonite.

There was a large decrease in cobalt sorption by montmorillonite as the pH decreased from pH 7.0 to 4.5. Below pH 4.0 there was only a very small further decrease in

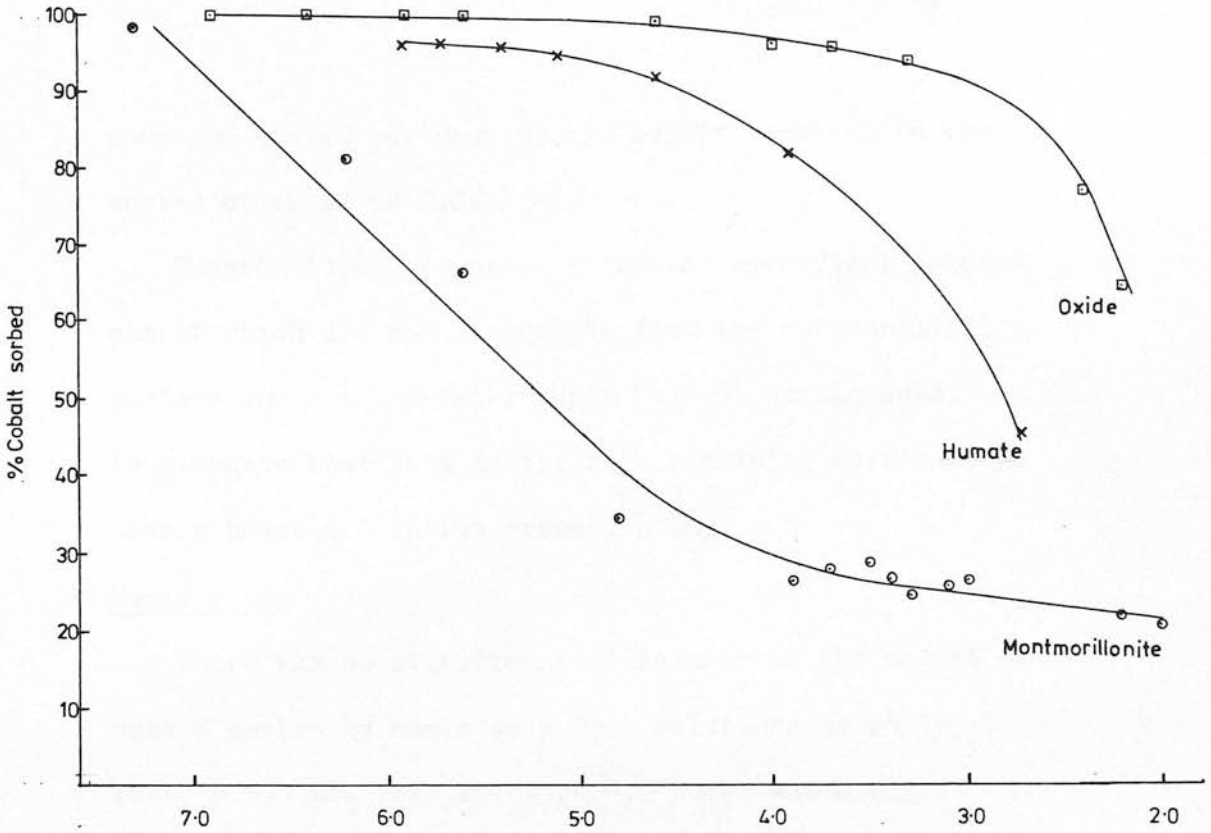


FIG. 6.4

Effect of solution pH on cobalt sorption by soil constituents.

Initial soln. Co concn. - Mont.: 0·05 µg/ml; Humate: 0·2 µg/ml; Oxide: 2·0 µg/ml

Background electrolyte - 0·01 M $CaCl_2$

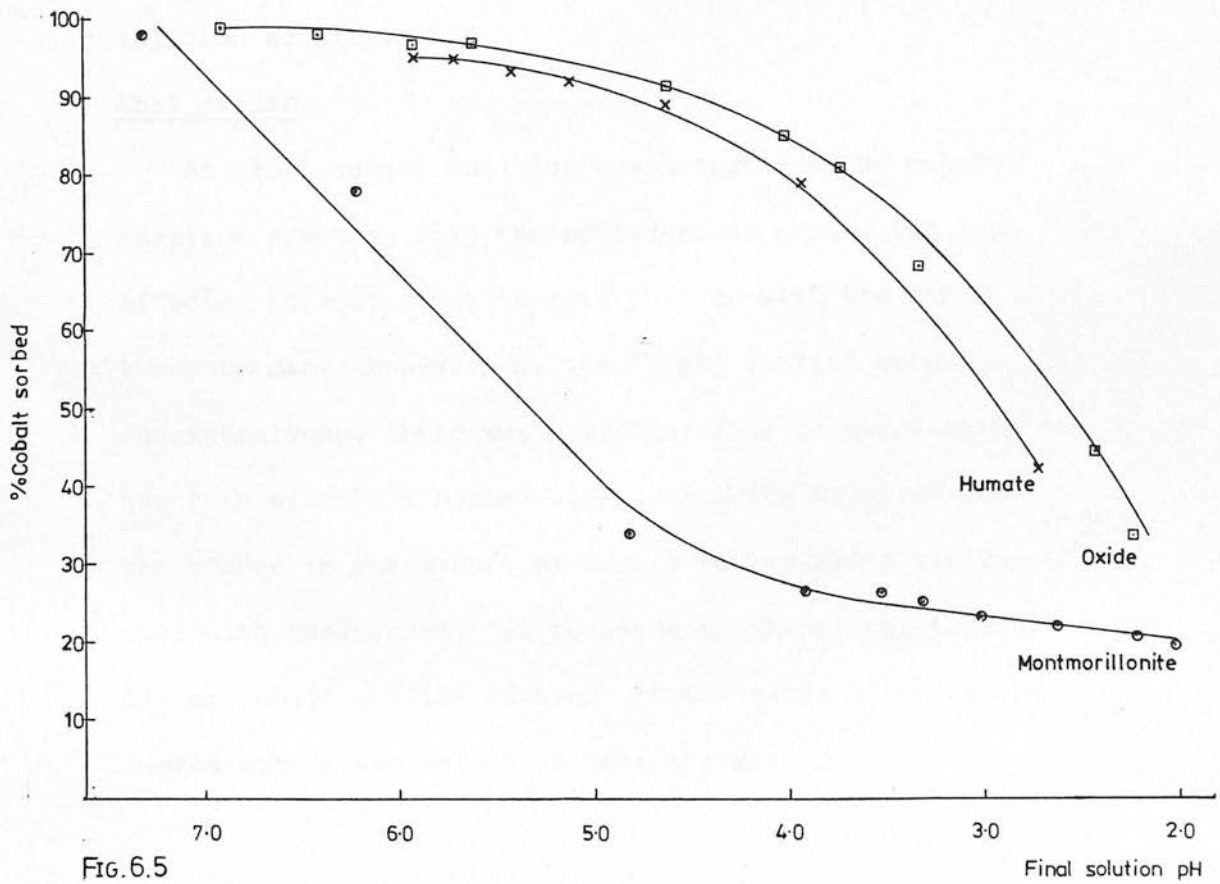


FIG. 6.5

Effect of solution pH on cobalt sorption by soil constituents.

Initial soln. Co concn.- Mont.: 0·2 µg/ml; Humate: 0·8 µg/ml; Oxide: 8·0 µg/ml

Background electrolyte - 0·01 M $CaCl_2$

sorption and 20 per cent of the cobalt remained in the sorbed state at pH 2.0.

Hodgson (1960) reported a form of specifically-bound cobalt which did not dissociate from the montmorillonite surface and was non-extractable by 2.5% acetic acid. It is probable that this is the form remaining sorbed at pH levels below 4.0 in the present study.

Humic acid.

There was no significant difference in the amount of cobalt sorbed by humic acid from solutions at pH levels above 4.5. However, below pH 4.5 there was a significant decrease in the quantity of cobalt sorbed with decreasing solution pH.

Kerndorff and Schnitzer (1980) also reported a decrease in cobalt sorption by humic acid with an increase in solution acidity.

Soil oxides.

At 'low' cobalt solution concentrations the cobalt sorption reaction with the soil-derived oxides was less affected by a decrease in soil pH than with the other two sorbents. However, at the 'high' initial cobalt concentrations, there was a greater rate of decrease in the quantity of cobalt sorbed with decreasing solution pH, the change in the amount of cobalt sorbed being similar to that with humic acid. It is evident, therefore, that at higher cobalt surface coverage on the oxide material the sorbed cobalt was held with less energy.

Loganathan et al. (1977) reported a small increase in cobalt sorption by δ-MnO_2 from pH 4.0 to 6.5; with an abrupt increase in the extent of sorption at pH levels above 6.5.

Forbes et al. (1976) observed that the specific sorption of cobalt by goethite increased from 8 per cent to 78 per cent of the solution cobalt sorbed, with an increase in solution pH from 6.4 to 8.0.

6.2.3 SORPTION ISOTHERMS

Soils.

Figures 6.6 and 6.7 present the cobalt sorption isotherms for 18 soils from the south-east of Scotland. The results of the chemical and physical analyses of these soils are shown in Table 4.1 of Chapter 4. The desorption of native cobalt into solution is shown on the isotherms as negative sorption and thus the sorption in the positive part of the isotherms measures the soils' ability to sorb added cobalt. The presence of excess calcium in solution supresses the sorption of cobalt by the cation exchange sites and thus the cobalt is held by specific sorption processes.

The sorption isotherms in Figures 6.6 and 6.7 are rectilinear, but it should be noted that, because the cobalt concentration range used was very small, the isotherms represent only a small portion of the isotherms obtained by using a wider range of concentrations. If higher cobalt concentrations were used in the sorption then a curvilinear isotherm would be obtained eg Tiller et al. (1969). The isotherms obtained

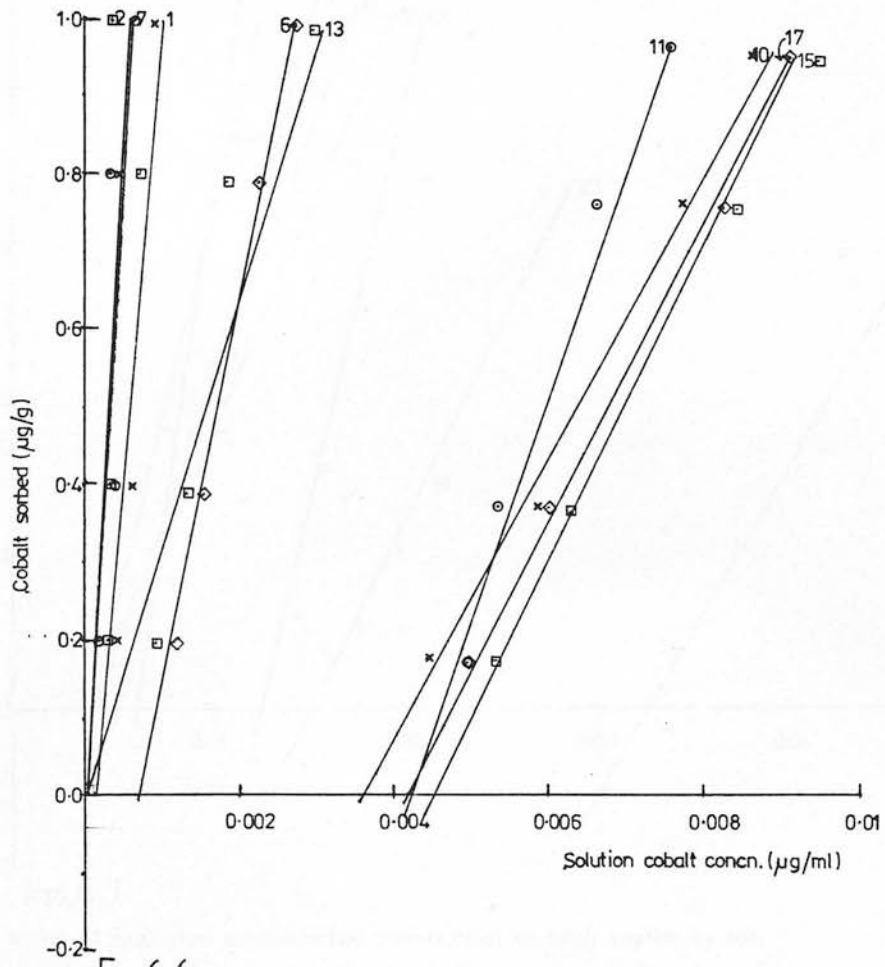


FIG. 6.6

Effect of equilibrium solution cobalt concentration on cobalt sorption by soil.

Sorption points measured for soils 2, 13, 15. □

" " " " " 7, 11. ○

" " " " " 1, 10. ×

" " " " " 6, 17. ◇

For clarity individual sorption points for cobalt sorption below 0·1 µg/g are not shown.

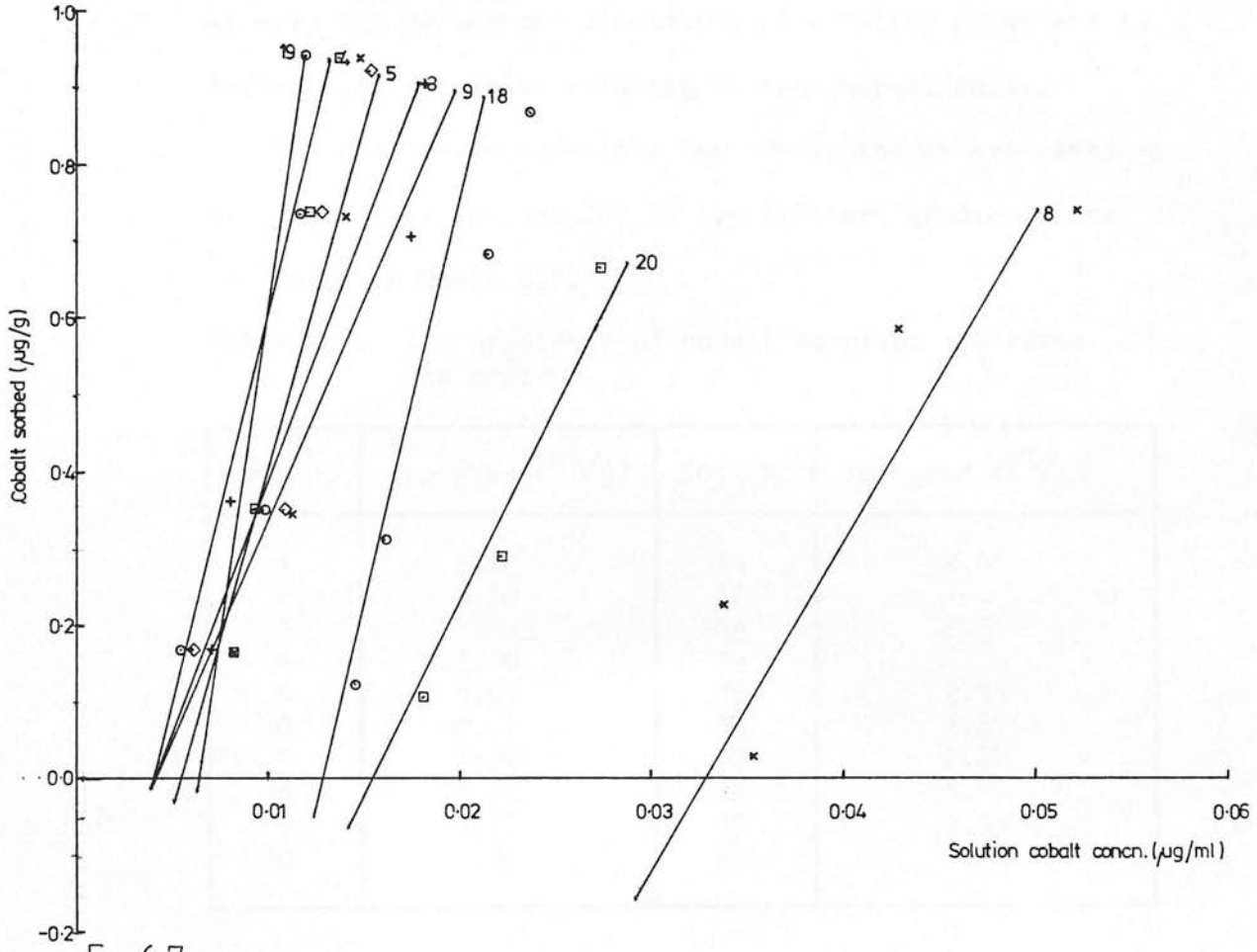


FIG. 6.7

Effect of equilibrium solution cobalt concentration on cobalt sorption by soil.

Sorption points measured for soils 19, 20. □
" " " " " 4, 18. ○
" " " " " 3, 8 ×
" " " " soil 5. ◇
" " " " " 9. +

For clarity individual sorption points for cobalt sorption below 0·1 µg/g (0·0 µg/g for soil 8) are not shown.

in this study comprise the initial steep portions of such isotherms. They therefore represent cobalt sorption at very low percentage occupation of sorption sites and so reflect the situation existing in most normal soils.

The regression equations for the isotherms are given in the appendices and the log of the isotherm gradients are presented in Table 6.1.

Table 6.1. Log gradients of cobalt sorption isotherms in soils

SOIL NO	log grad ($^{ml}/_{g}$)	SOIL NO	log grad ($^{ml}/_{g}$)
1	3.07	11	2.46
2	3.30	12	-
3	1.82	13	2.51
4	2.00	14	-
5	1.94	15	2.32
6	2.69	16	1.87
7	3.22	17	2.28
8	1.63	18	1.84
9	1.76	19	1.93
10	2.26	20	1.69

Montmorillonite.

The cobalt sorption isotherm for montmorillonite was curvilinear indicating that, as the amount of cobalt added to the system was increased, the proportion of the added cobalt sorbed by the clay decreased (Fig. 6.8).

Figure 6.9 shows the extent to which sorbed cobalt could be desorbed back into 0.01 M $CaCl_2$ solution. It is evident that the sorption process was not easily reversible and that cobalt was being 'fixed' by the clay mineral to some extent.

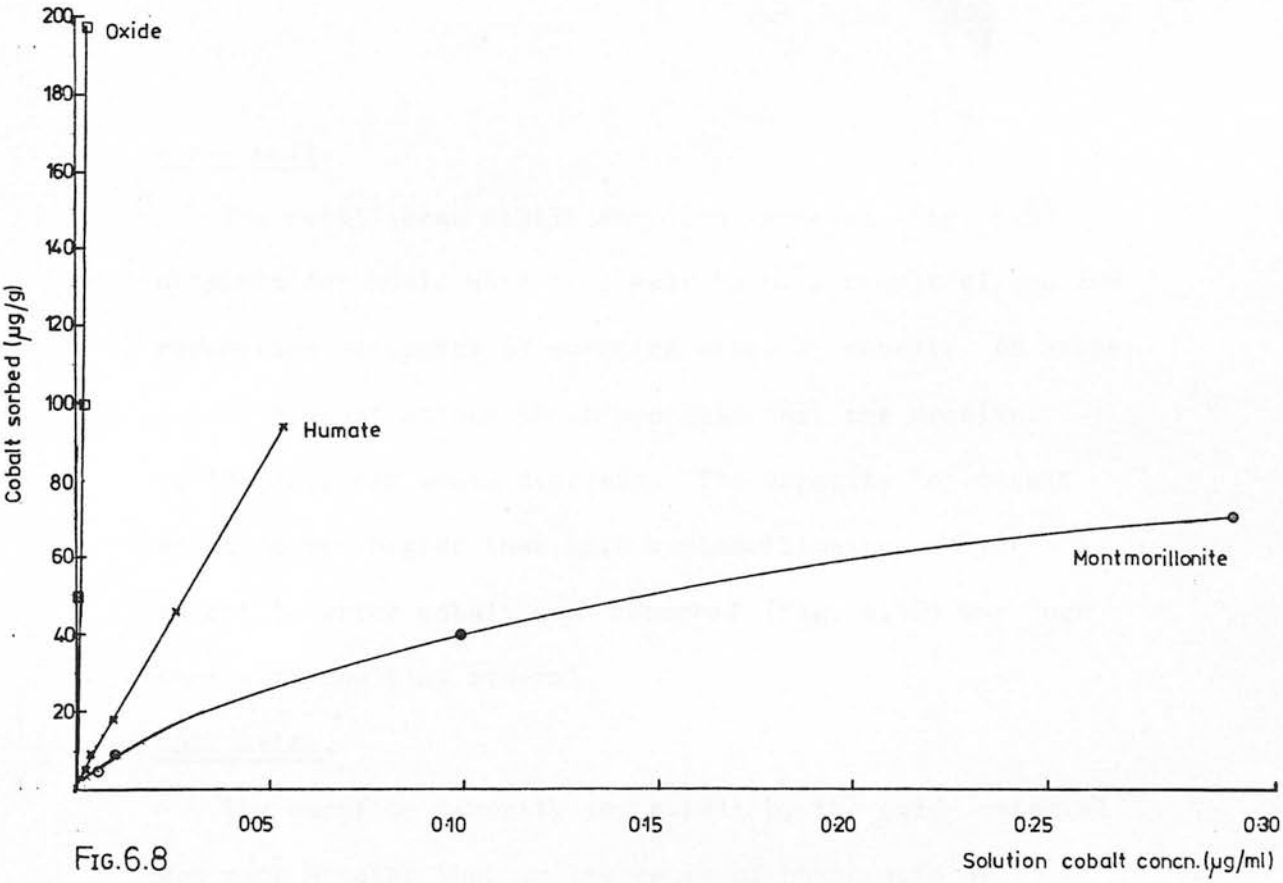


FIG. 6.8

Effect of equilibrium solution cobalt concentration on cobalt sorption by soil constituents.
Background electrolyte - 0·01M $CaCl_2$
Final soln. pH - 6·0 - 6·2

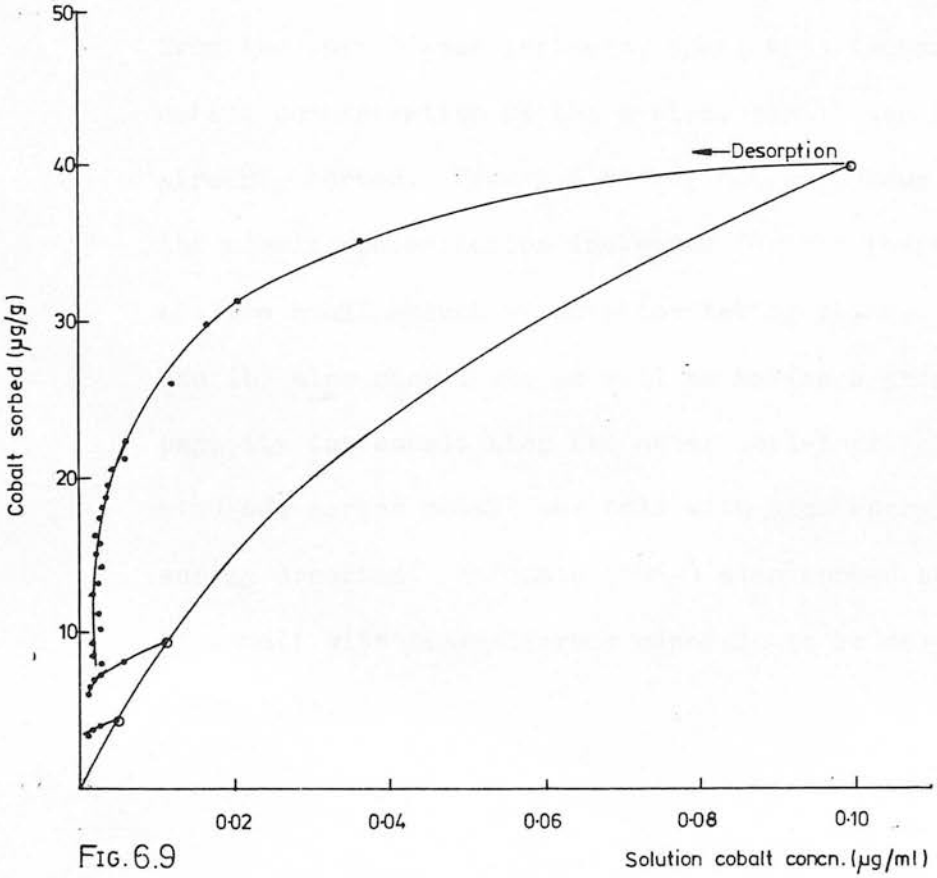


FIG. 6.9

Effect of equilibrium solution cobalt concentration on cobalt sorption by and desorption from montmorillonite.
Background electrolyte - 0·01M $CaCl_2$; Final soln. pH - 6·2

Humic acid.

The rectilinear cobalt sorption isotherm (Fig. 6.8) obtained for humic acid is likely to be a result of the low percentage occupancy of sorption sites by cobalt. At higher cobalt concentrations it is probable that the gradient of the isotherm would decrease. The capacity for cobalt sorption was higher than with montmorillonite and the extent to which cobalt was desorbed (Fig. 6.10) was less than with the clay mineral.

Soil oxide.

The sorption capacity for cobalt by the oxide material was much greater than in the cases of humic acid or montmorillonite (Fig. 6.8). McKenzie (1967) showed that manganiferous nodules extracted from soil had a remarkably strong affinity for solution cobalt. Figure 6.11(a) indicates, from the curvilinear isotherm, that, with increasing cobalt concentration in the system, cobalt was less strongly sorbed. Figure 6.11(b), however shows that as the cobalt concentration increased further there was still a small amount of sorption taking place. Figures 6.11(a) and (b) also show that, as well as having a greater sorption capacity for cobalt than the other soil-forming materials studied, sorbed cobalt was held with high energy and not easily desorbed. McKenzie (1967) also showed the reaction of cobalt with manganiferous minerals to be only partly reversible.

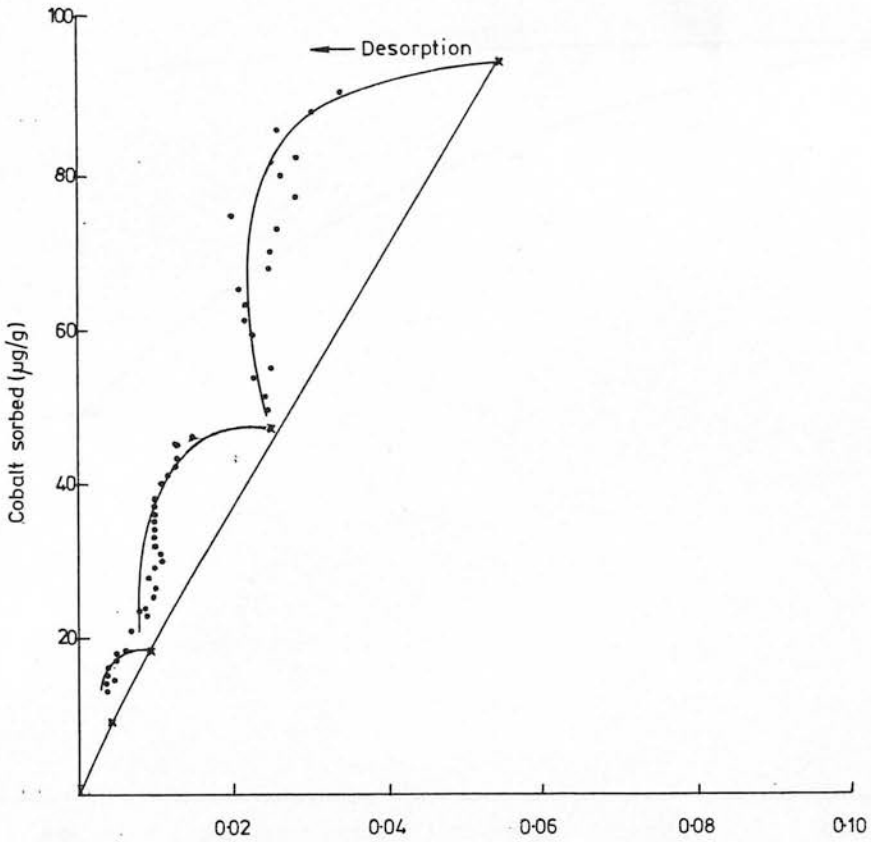


FIG. 6.10

Effect of equilibrium solution cobalt concentration on cobalt sorption by and desorption from humic acid.

Background electrolyte - 0·01M $CaCl_2$; Final soln. pH - 6·0

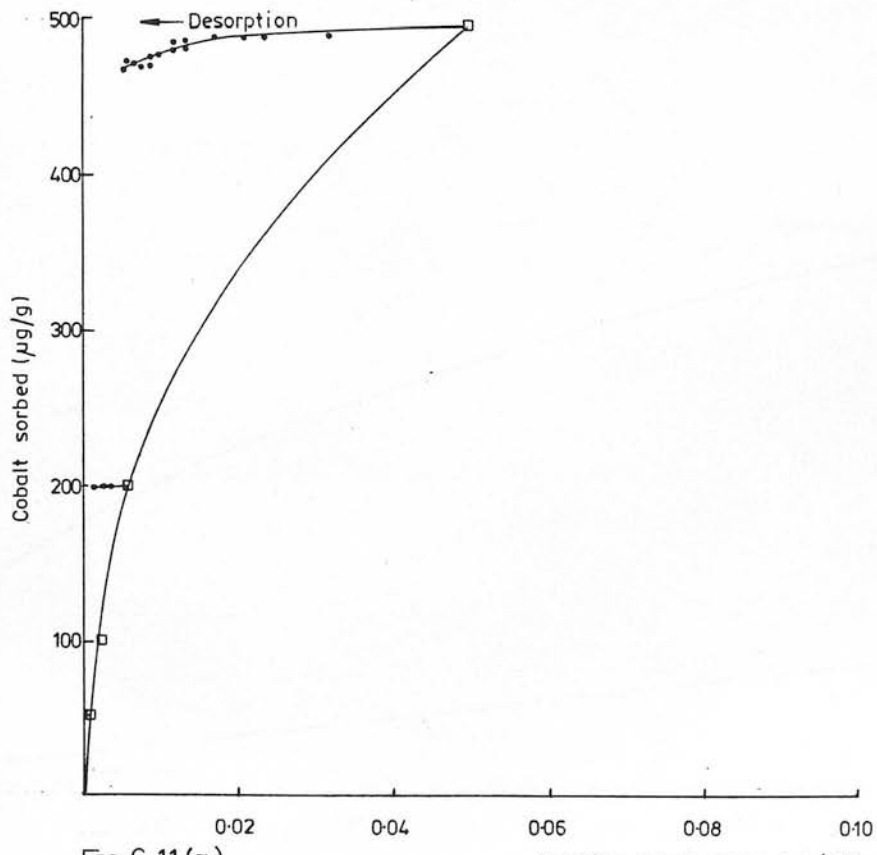


FIG. 6 11 (a)

Effect of equilibrium solution cobalt concentration on cobalt sorption by and desorption from soil oxide (low concn. range).

Background electrolyte - 0·01M $CaCl_2$; Final soln pH - 6·0

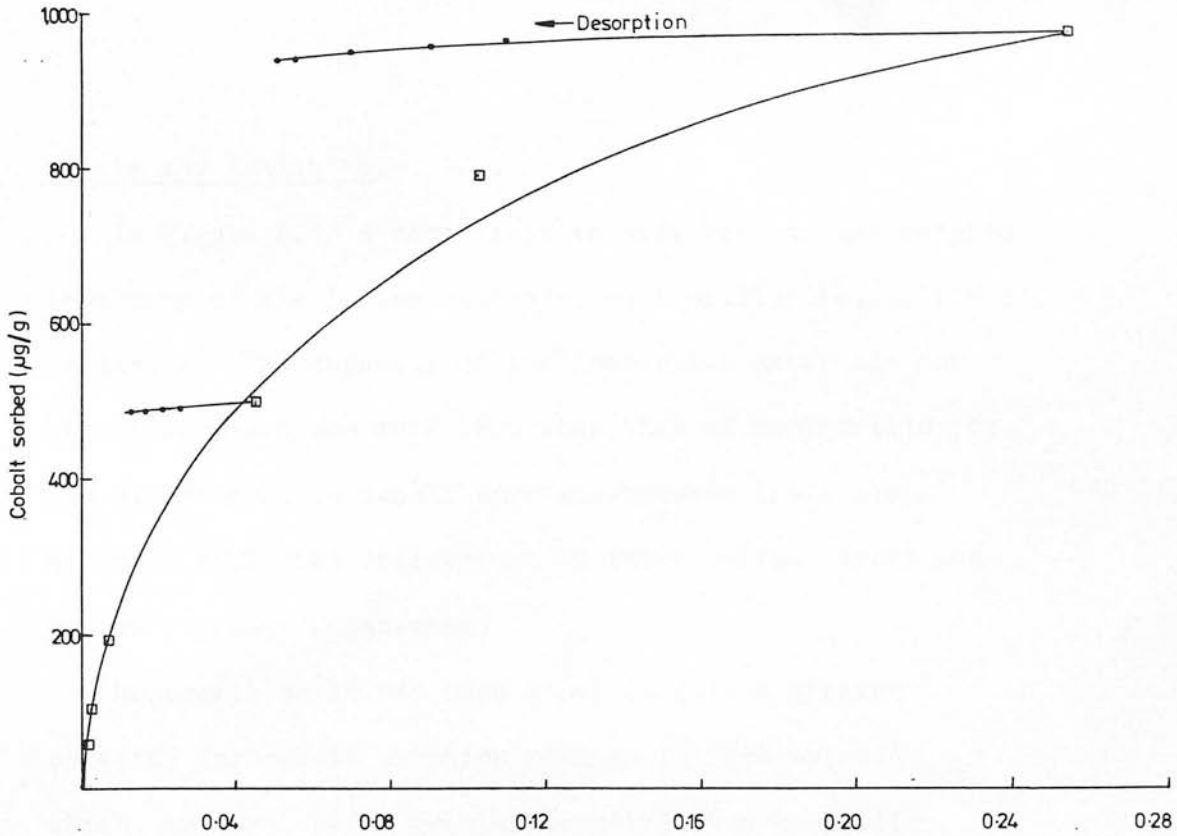


FIG. 6.11(b)

Effect of equilibrium solution cobalt concentration on cobalt sorption by and desorption from soil oxide (high concn. range).
Background electrolyte - 0·01M $CaCl_2$; Final soln. pH - 6·0

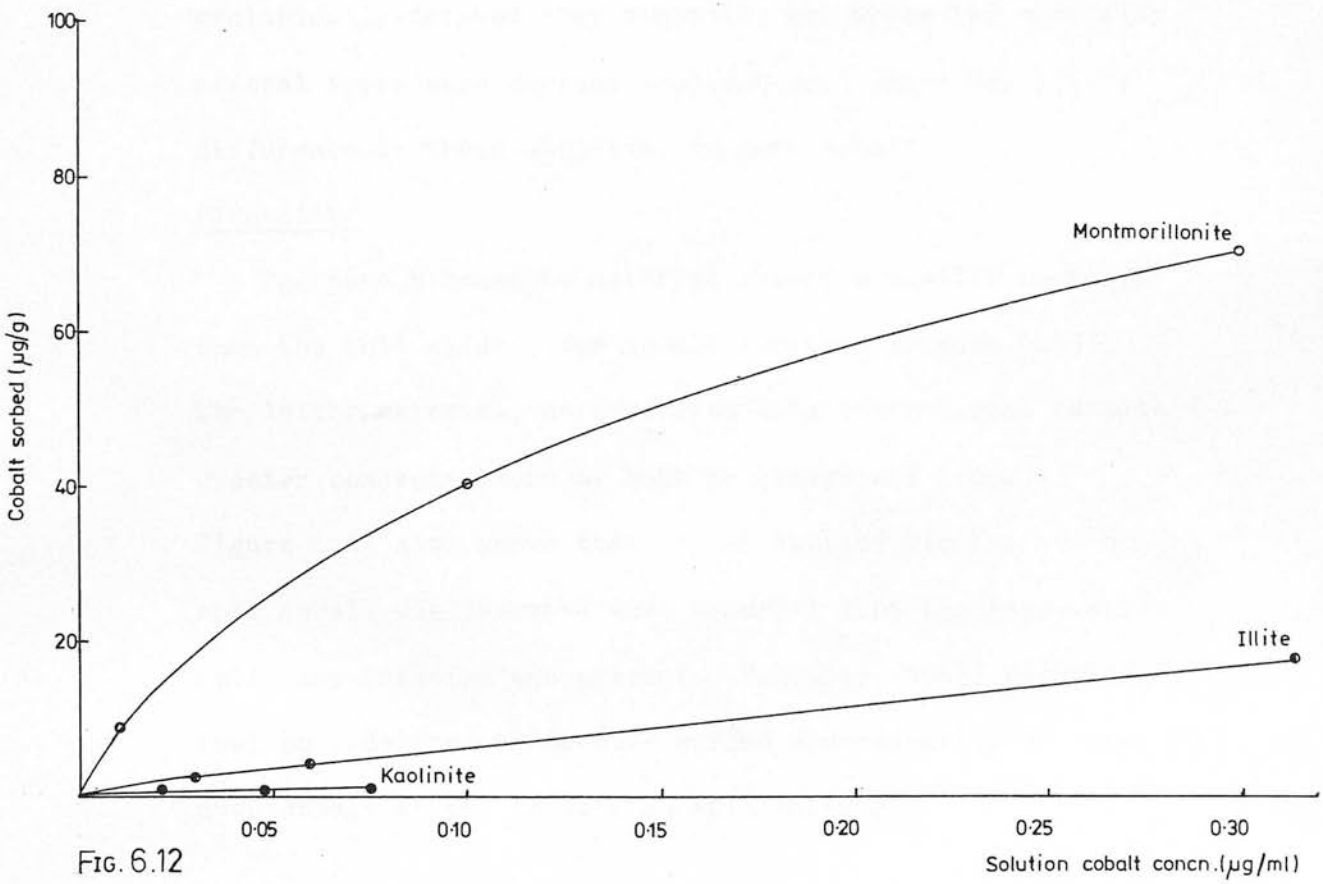


FIG. 6.12

Effect of equilibrium solution cobalt concentration on cobalt sorption by clay minerals.
Background electrolyte -0·01M $CaCl_2$; Final soln. pH - 6·2 – 6·4

Illite and Kaolinite.

In Figure 6.12 a comparison is made between the sorption isotherms of the 3 clay minerals, montmorillonite, illite and kaolinite. The capacity of the latter two materials for cobalt sorption was much less than that of montmorillonite. The differences in cobalt sorption between these clay minerals reflected differences in their surface areas and cation exchange capacities.

Montmorillonite has been shown to have a greater capacity for cobalt sorption than an illitic subsoil, which, in turn, had a greater capacity than kaolinite (Andersson, 1977).

Tiller et al. (1963) also noted considerable differences in the amounts of cobalt specifically sorbed by a range of geologically-derived clay minerals, but where the same clay mineral types were derived from sub-soil there was little difference in their abilities to sorb cobalt.

Birnessite.

The pure birnessite material showed a smaller capacity, than the soil oxides, for cobalt sorption (Figure 6.13). The latter material, derived from soil concretions, contained greater concentrations of both manganese and iron. Figure 6.13 also shows that the ability of birnessite to sorb cobalt was lessened when material from the associated soil clay fraction was present. McKenzie (1967) reported that soil-derived birnessite sorbed approximately 20 times as much cobalt as the associated soil material.

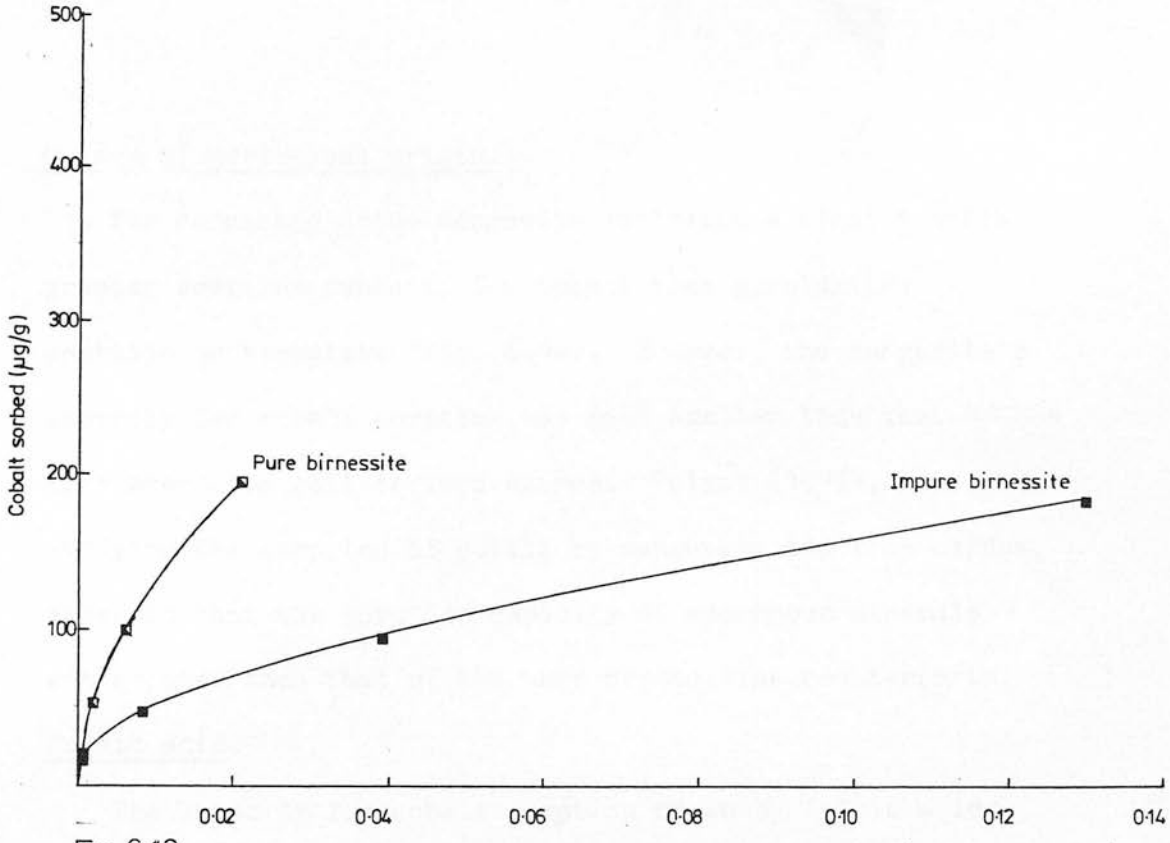


FIG. 6.13

Effect of equilibrium solution cobalt concentration on cobalt sorption by soil birnessite.
Background electrolyte - 0·01 M $CaCl_2$; Final soln. pH - 6·3 - 6·4

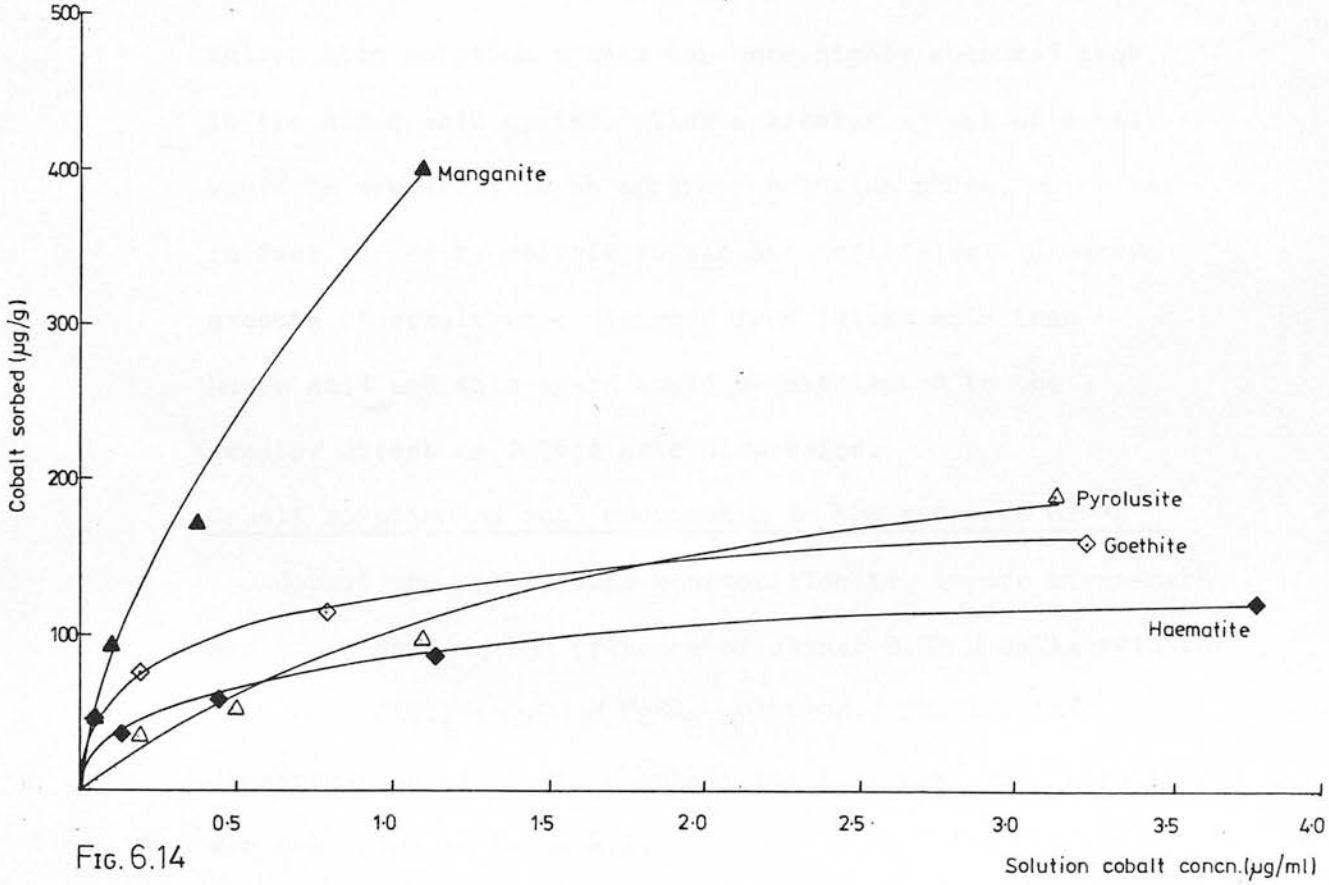


FIG. 6.14

Effect of equilibrium solution cobalt concentration on cobalt sorption by geologically derived oxides.
Background electrolyte - 0·01 M $CaCl_2$; Final solution pH - 6·1 - 6·3

Oxides of geological origin.

The manganese oxide manganite exhibited a significantly greater sorption capacity for cobalt than pyrolusite, goethite or haematite (Fig. 6.14). However, the manganite's capacity for cobalt sorption was much smaller than that of the more amorphous soil-derived oxides. Polgar (1975), in studying the sorption of cobalt by manganese and iron oxides, observed that the sorption capacity of amorphous minerals was greater than that of the more crystalline counterparts.

Fulvic acid.

The capacity for cobalt sorption shown by fulvic acid (Fig. 6.15) appeared to be smaller than in the humic acid system (Fig. 6.10). This was probably attributable to a greater dispersion of fulvic acid, than humic acid, into solution after centrifugation. The supernatant in the fulvic acid sorption system was more highly coloured than in the humic acid system. Thus a greater amount of cobalt would be measured, in an apparent solution phase, which was in fact sorbed by soluble fulvic acid molecules. Greater amounts of cobalt were desorbed from fulvic acid than humic acid and this again could be attributed to the greater extent of fulvic acid dispersion.

Cobalt sorption on soil components in the presence of Mg^{2+}

Cobalt was sorbed onto montmorillonite, impure birnessite and humic acid in the presence of either 0.02 M $CaCl_2$ solution or 0.01 M $CaCl_2$ + 0.01 M $MgCl_2$ solution. The initial concentration of solution cobalt was 0.02 ppm. The results are presented in Table 6.2.

Table 6.2. Effect of solution Mg^{2+} on cobalt sorption. Results are the mean of 2 replicates.

SORBENT	$pHCaCl_2$*	Cobalt sorbed ($\mu g/g$)	
		$CaCl_2$	$CaCl_2 + MgCl_2$
Montmorillonite	6.9-7.1	1.96	1.58
Birnessite (imp)	6.0	15.66	15.46
Humic acid	6.0	15.09	15.09

*$pHCaCl_2$ is the final pH of the sorbing solution

The presence of magnesium ions in solution decreased the sorption of cobalt by montmorillonite, but not by the other two materials.

Hodgson (1960) reported that magnesium had little effect in decreasing the specific sorption of cobalt on montmorillonite, whereas copper, zinc, iron and nickel did. However, the concentration of magnesium used was 2,000 times less than in the present study.

The effect of ethanol on cobalt sorption by montmorillonite in the presence of solution magnesium is demonstrated in Table 6.3.

Table 6.3. Effect of ethanol on cobalt sorption in the presence of solution Mg. Results are the mean of two replicates.

Final $pHCaCl_2$	Co sorbed ($\mu g/g$)	
	$CaCl_2$	$CaCl_2 + MgCl_2$
5.6-5.7	1.97	1.76

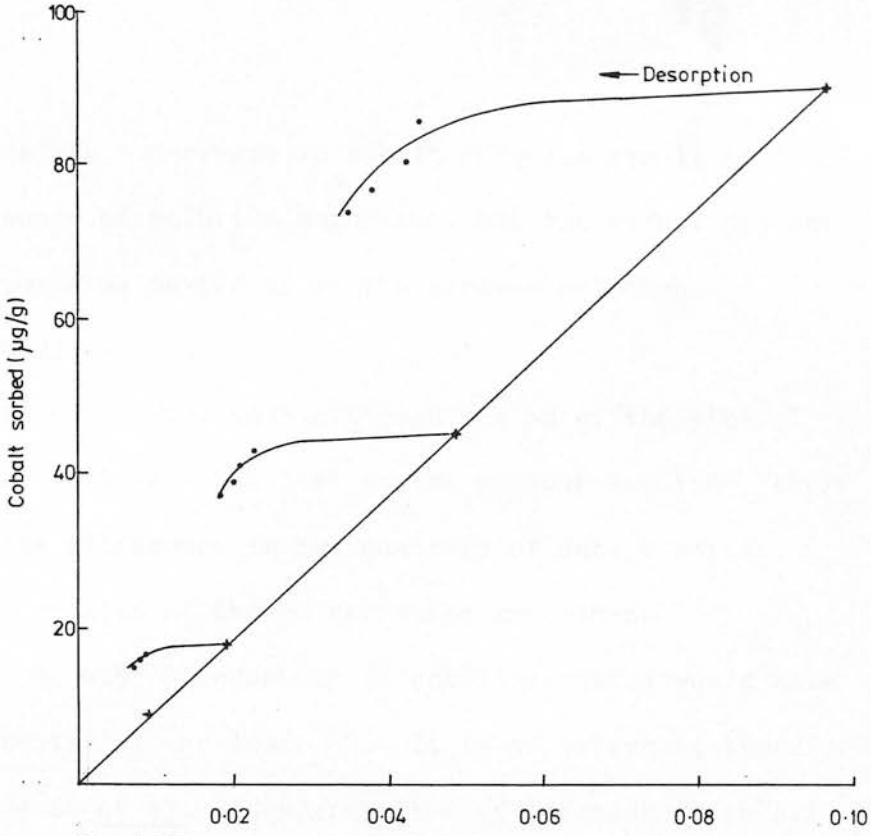


FIG. 6.15

Effect of equilibrium solution cobalt concentration on cobalt sorption by and desorption from fulvic acid.

Background electrolyte - 0·01M $CaCl_2$; Final solution pH - 5·8 – 6·0

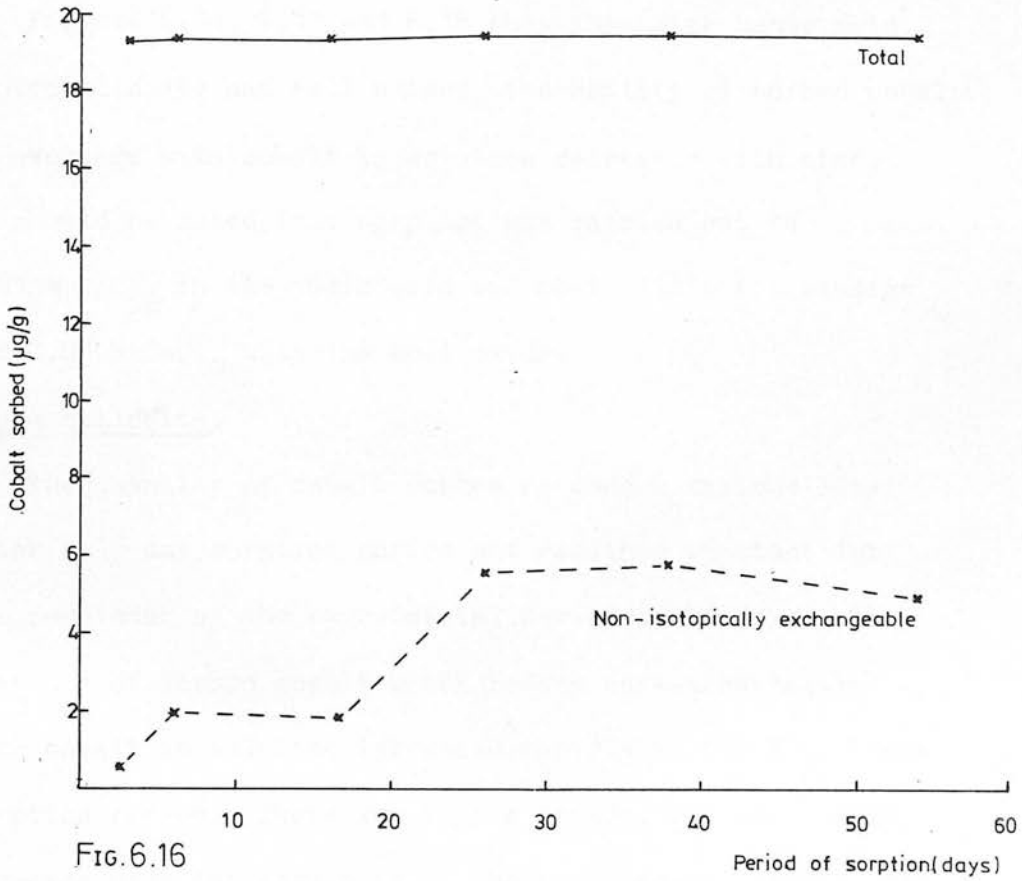


FIG. 6.16

Effect of time on the total and non-isotopically exchangeable fraction of cobalt sorption by humic acid.

There was a decrease in cobalt sorption resulting from the presence of solution magnesium, but the effect did not appear to be as marked as in the aqueous solution (Table 6.2).

It is noteworthy that although the pH of the ethanol solution was lower than that of the aqueous solution, there was little difference in the quantity of cobalt sorbed. From the results of the pH variation experiment (Figs. 6.4, 6.5) a reduction in cobalt sorption would have been expected at the lower pH. It is of interest, therefore, that Hodgson et al. (1964) reported an increase in cobalt uptake by montmorillonite when sorption was carried out in ethanol solution.

6.2.4. ISOTOPIC EXCHANGEABILITY OF COBALT SORBED ON SOIL MATERIALS

Figures 6.16, 6.17 and 6.18 show that with humic acid, montmorillonite and soil oxides, the ability of sorbed cobalt to exchange with cobalt in solution decreases with time. It should be noted that sorption was carried out in 0.01 M $CaCl_2$ in the humic acid and montmorillonite studies and 0.05 M $CaCl_2$ with the soil oxide.

Montmorillonite.

The quantity of cobalt sorbed reached a maximum level after a 15 day sorption period and remained constant for the remainder of the experimental period of 54 days. The fraction of sorbed cobalt which became non-exchangeable with cobalt in solution increased rapidly in the 3 to 6 day sorption period. There was then a steady, but less rapid, increase over the remainder of the experiment. After

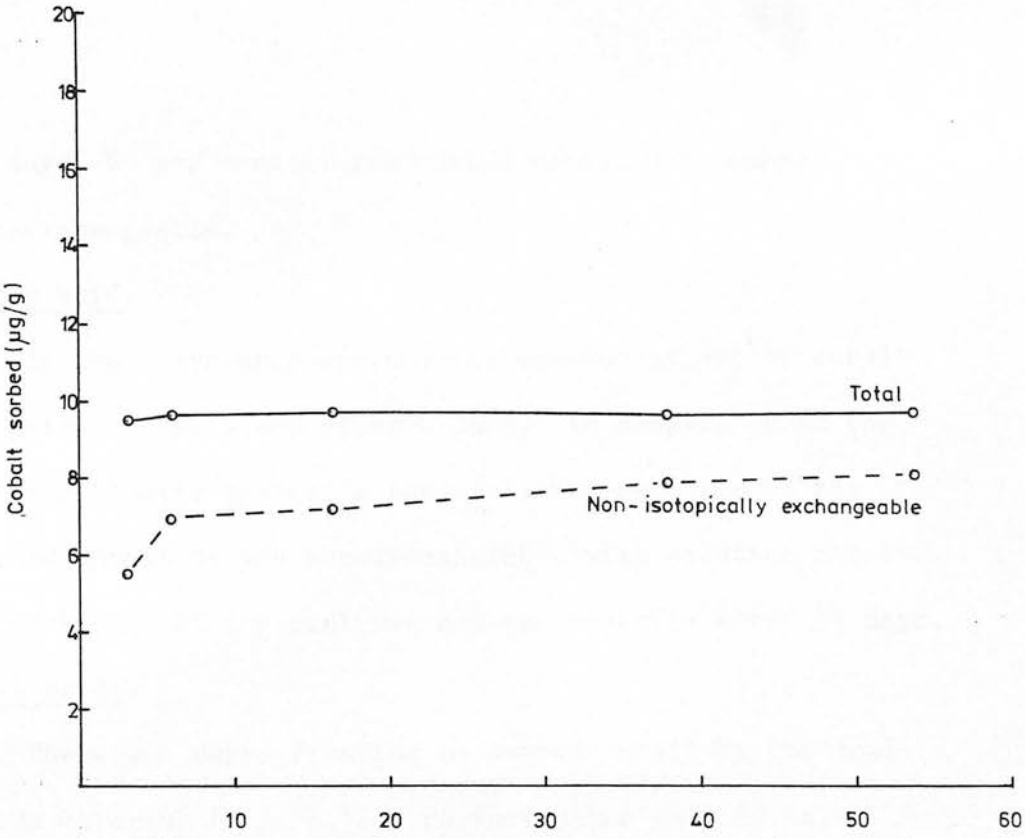


FIG. 6.17

Effect of time on the total and non-isotopically exchangeable fraction of cobalt sorption by montmorillonite.

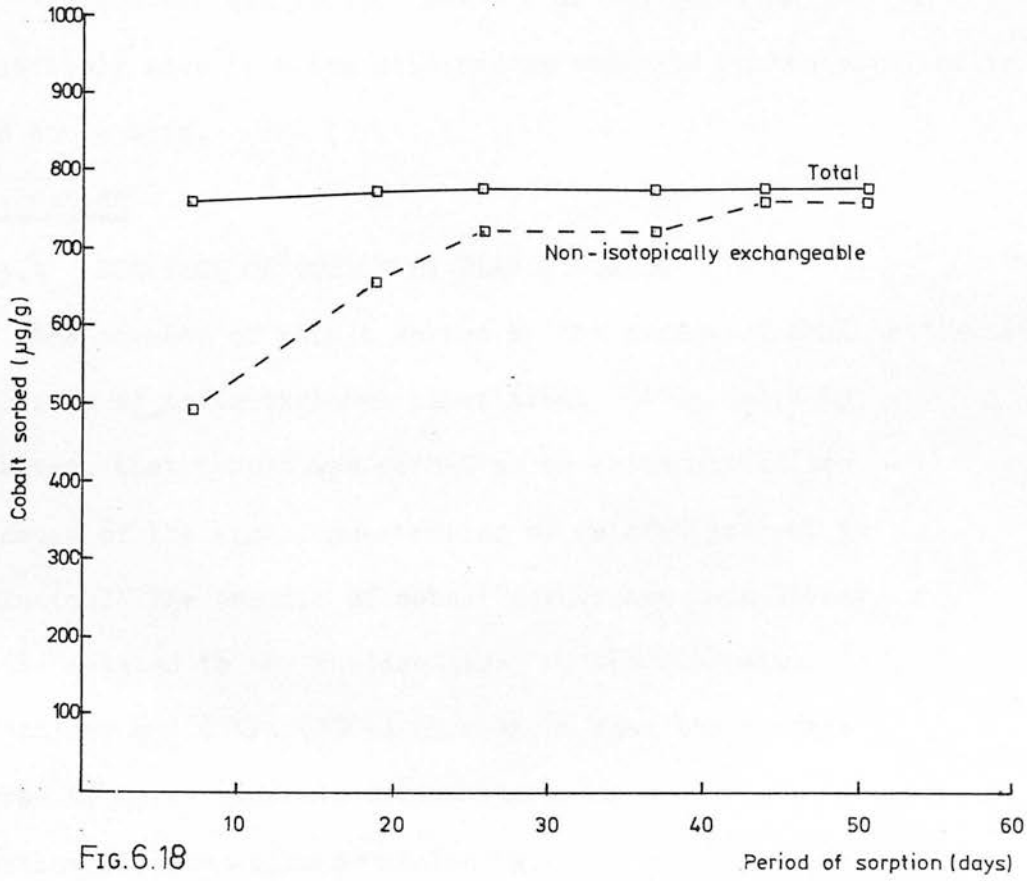


FIG. 6.18

Effect of time on the total and non-isotopically exchangeable fraction on cobalt sorption by soil oxide.

54 days, 83 per cent of the sorbed cobalt had become non-exchangeable.

Humic acid.

In the humic acid system, the maximum amount of cobalt sorption was attained after 6 days. In comparison to the montmorillonite system, a far smaller proportion of the sorbed cobalt became non-exchangeable with solution cobalt, so that only 25 per cent was non-exchangeable after 54 days.

Soil oxide.

There was rapid fixation of sorbed cobalt by the soil oxide material (Fig. 6.18), so that after only 26 days, 95 per cent of the sorbed cobalt was non-exchangeable. This proportion continued to increase during the remainder of the sorption period.

The maximum quantity of total specific sorption was relatively slow in being attained as compared to montmorillonite and humic acid.

6.3 Discussion

6.3.1 SORPTION OF COBALT BY CLAY MINERALS

The amounts of cobalt sorbed by the 3 clay minerals reflected the size of their exchange capacities. It is unlikely, however, that cobalt was sorbed as an exchangeable ion because of the high concentration of calcium present in solution. The amounts of cobalt sorbed are more likely to be related to the surface areas of the minerals. Greenland and Quirk (1964) have shown that the surface areas of these minerals follow the order montmorillonite > illite > kaolinite.

The different behaviour between clay minerals which are geologically or soil-derived was investigated by Tiller et al. (1963). Although geologically-derived montmorillonite sorbed more cobalt than kaolinite, there was little difference in the sorption behaviour of the two clay minerals when derived from sub-soil. It was suggested that the extent of structural defects present in clay minerals, especially in samples from soil, were of importance for their ability to sorb cobalt. Thus, minerals of different types could behave similarly in their extent of cobalt sorption. The results of Hodgson et al. (1969) apparently supported this hypothesis. They treated geological and soil clays with lithium oxalate and sodium oxalate in order to remove iron, after organic matter had been removed with hydrogen peroxide. In general, there was little effect on cobalt sorption from these treatments and again they noted a remarkable similarity amongst clay fractions of widely divergent soil types in their reactivity with cobalt.

Although the treatments, on the soil clays, in some cases removed significant amounts of manganese their results show that there were still adequate amounts present to sorb substantial amounts of cobalt. The results of the present study show, (Fig. 6.13) that a birnessite mineral containing 1.9% Fe and 3% manganese could sorb over 10 times as much cobalt as the clay minerals. Thus a small amount of manganese oxide on the clay mineral surface can make a large contribution to cobalt sorption.

It seems likely that there would be a similarity in cobalt sorption capacity in soil-derived clay minerals as a result of surface oxide coatings. The large differences observed in the extent of reaction with cobalt shown by the 3 clay minerals in the present experiment may not be shown by these minerals in the soil fabric.

As shown in Figure 6.1, the time taken for cobalt sorption by montmorillonite to reach equilibrium was comparatively slow. Figure 6.17 shows that sorption required over 15 days to reach equilibrium. Hodgson (1960) observed that there was initially a fast specific sorption rate between cobalt and montmorillonite, followed by a slower reaction rate. He attributed the initial rapid rate of sorption to chemisorption on the mineral surface, and the second slow reaction to entry into the montmorillonite crystal lattice.

The results of the present study appear to show that more than two specific sorption reactions take place between cobalt and montmorillonite. The results of the experiment examining the effect of pH on cobalt sorption showed that, although there was a large decrease in cobalt sorption with decreasing pH, 20 per cent of the cobalt added remained sorbed at pH 2.0. This contrasts with the result of the isotopic exchange experiment, carried out at the same cobalt concentration, in which 45 per cent of the specifically sorbed cobalt was found to be non-isotopically exchangeable after a 48 hour sorption period. It would

therefore appear that a considerable amount of the cobalt sorbed by the clay is not exchangeable with cobalt in solution, but can be desorbed by a reduction in solution pH. The cobalt remaining sorbed at pH 2.0 is likely to be comparable with the 'non-exchangeable' fraction observed in studies by Hodgson (1960) which was non-extractable by 2.5% acetic acid (pH 2.5). This fraction is considered to be comprised of cobalt that has entered the crystal lattice of the mineral.

Figure 6.17 also shows that, with time, the percentage of non-isotopically exchangeable sorbed cobalt increased. Because there was no increase in the total quantity of sorbed cobalt, there must have been a change in form of the sorbed cobalt. This may have resulted from the non-isotopically exchangeable adsorbed cobalt increasing in concentration, or further migration of adsorbed cobalt into the clay mineral lattice.

In studies by Hodgson (1960), the fraction of sorbed cobalt not extractable by acetic acid increased from 8 per cent, after 2 days, to 38 per cent after 30 days, implying that there was considerable diffusion of cobalt into the clay mineral lattice over this period. An equivalent increase in the concentration of cobalt held within the lattice, in the present experiment, would necessitate the entry of both isotopically exchangeable and non-isotopically exchangeable surface-held cobalt into the mineral lattice.

At the 48 hour sorption period, approximately 55 per cent of the sorbed cobalt was isotopically exchangeable. This is likely to be cobalt adsorbed on the surface at hydroxyl groups. The effect of increasing H^+ concentration would be to replace cobalt held at these sites. The fraction of cobalt which was held on the surface in a non-isotopically exchangeable form was possibly entering into surface precipitation reactions. These reactions would also be susceptible to a decrease in solution pH.

The former type of surface reaction between cobalt and montmorillonite was proposed by Hodgson, Geering and Fellows (1964), who reported that the reaction of cobalt with montmorillonite was endothermic and occurred at the surface hydroxyls by exchange with weakly dissociable hydrogen ions. De Mumbrum and Jackson (1956), using infra-red absorption techniques, reported a decrease in the hydroxyl bond absorption intensity of montmorillonite, vermiculite and kaolinite when copper and zinc were sorbed. This indicated that a reaction was taking place between metal ions and clay mineral octahedral hydroxyl groups.

Evidence for this type of bonding between cobalt and kaolinite, at solution pH < 5.0, was reported by Dillard and Koppelman (1982) using X-ray photoelectron spectroscopy. However, at solution pH above 7.8 the cobalt bonding was of a more ionic nature and was consistent with the formation of $Co(OH)_2$. In the pH range 5 to 7, both processes were taking place. It should be noted that the concentrations of cobalt used by Dillard and Koppelman were far in excess of

those used in the present study. However, as a result of the relatively high concentration of cobalt likely to be found at the montmorillonite-solution interface, it is possible that some precipitation reactions between cobalt and surface hydroxide groups take place.

The presence of a third type of bonding produced by migration of cobalt into the mineral lattice, was indicated by the result of introducing a relative excess quantity of magnesium into solution. This caused a 20 per cent decrease in cobalt sorption by montmorillonite (Table 6.2). Magnesium has a smaller ionic radius (0.78Å) than cobalt (0.82Å) and it can compete more effectively than calcium (ionic radius 1.06Å) for entry into the vacant octahedral sites in montmorillonite.

McKenzie (1963), on measuring the immobilisation of metal ions sorbed by montmorillonite by successive heating and wetting treatments, found that the extent of migration of metal ions into the mineral lattice was dependent on the ionic radius. Thus metal ions with radii greater than 0.85Å were not appreciably immobilised.

It was observed, in the present study, that there was an unexpectedly high level of cobalt sorption by montmorillonite when carried out in alcohol solution (Table 6.3). This was possibly a result of the unhydrated cobalt ions in ethanol solution having a greater ability to enter into the vacant octahedral sites, in the montmorillonite crystal lattice, than the hydrated ions present in aqueous solution.

The hydrated ions would require energy of dehydration before being able to enter the mineral lattice. Table 6.3 also shows that the presence of magnesium ions in the ethanol solution caused a decrease of 10 per cent in the total amount of cobalt sorbed from where no magnesium was present. This is further evidence that sorbed cobalt migrates into the clay mineral lattice. Hodgson, Geering and Fellows (1964) also observed an enhancement of specific sorption of cobalt by montmorillonite when carried out in alcohol solution. However, these authors proposed that this resulted from changes in the clay mineral surface structure in the presence of alcohol.

The effect of increasing solution calcium concentration to above 0.01 M was to significantly decrease the amount of cobalt being sorbed by montmorillonite (Figs. 6.2, 6.3). Hodgson, Geering and Fellows (1964) proposed that the effect of increasing calcium concentration was to decrease the chemical activity of cobalt in solution, thus decreasing its sorption. It is likely that this phenomenon caused some of the decrease in cobalt sorption observed in the present study. However, the increasing solution calcium concentration would also cause greater flocculation of the clay mineral, resulting in a decrease in the surface area available for cobalt sorption. The high calcium concentrations would also cause cobalt to be excluded from the counter-ion population at the montmorillonite-solution interface and so decrease the quantity of cobalt able to sorb.

6.3.2 SORPTION OF COBALT BY IRON AND MANGANESE OXIDES OF SOIL AND GEOLOGICAL ORIGIN

The soil-derived oxide materials (ie birnessite and concretion oxides) exhibited a greater ability to sorb solution cobalt than any other material studied, including oxides of geological origin. The birnessite and concretion oxides, because of their formation under less stable conditions, would be of more amorphous form than the geological minerals, and would largely be present as surface coatings on silicate minerals. A larger surface area would therefore be available for cobalt sorption in the soil-derived compounds.

Although other oxides, such as aluminium oxide, would be present in the soil-derived oxides, manganese and iron oxide have been shown to have a greater capability for cobalt sorption than aluminium oxide (Tewari et al. (1972). The high affinity of manganese oxides for cobalt has also been widely reported (McKenzie, 1970; Loganathan et al. (1977); Means et al. 1978b). It can be assumed from the relatively large concentrations of manganese and iron in the soil-derived materials that manganese and iron oxides would play a dominant role in the sorption of cobalt.

The effect of increasing the solution ionic strength on cobalt sorption by the soil concretion oxides (Figs. 6.2, 6.3) was extremely small. The fact that there was a slightly greater effect on cobalt sorption at the 'higher' initial cobalt concentration indicates that the

consequences of increasing the calcium concentration were not due entirely to greater flocculation of the oxides or to a decrease in the chemical activity of cobalt in solution. If the decrease in cobalt sorption had been caused predominantly by these two factors then similar percentage decreases in cobalt sorption would have been obtained at the two different cobalt concentrations.

Cobalt bonding at high cobalt concentration is of lower energy than at low cobalt concentration. Thus calcium concentration has a proportionally greater effect on the more weakly bound specifically sorbed cobalt than that bound with higher energy. The calcium thus appeared to have a direct effect on the specific sorption reaction between cobalt and the oxide.

The effect of solution pH change on the sorption of cobalt by the concretion oxides was markedly different at the two different cobalt concentrations in the system (Figs. 6.4, 6.5). At lower surface coverage, there was little change in the quantity of cobalt sorbed with variation in solution pH, so that at pH 3.0, 90 per cent of the cobalt remained sorbed. However, at higher cobalt surface coverage, only 62 per cent of the cobalt was sorbed at pH 3.0. If the effect of decreasing solution pH had been solely the dissolution of the oxides then equivalent percentages of cobalt would be sorbed, at different cobalt concentrations, over the whole pH range. The solution pH, therefore, directly affected the specific sorption reaction between solution

cobalt and the oxide surface and did so to a greater extent than the solution calcium concentration.

The pH experiment was conducted at two different points on the cobalt sorption isotherm (Fig. 6.11(b)): firstly at the steep part of the slope where specific sorption was at higher energy and, secondly, at the shallower part of the slope where specific sorption took place at a comparatively lower energy. The cobalt sorbed at the lower energy level was more susceptible to desorption by a reduction in solution pH than specifically sorbed cobalt at the higher energy level. It is evident therefore that, as in the case with solution calcium concentration, solution hydrogen ion concentration directly affects the specific sorption reaction between cobalt and the soil oxides.

The specific sorption of cobalt by the soil oxides was highly irreversible, as shown by the desorption curves in Figs. 6.11(a) and 6.11(b). It is of note, however, that the irreversibility of the sorption reaction was as great at lower energy as at higher energy (Fig. 6.11(b)). This suggests that, over the period during which the cobalt held at lower energy sites was being desorbed, there was a process taking place simultaneously which resulted in this cobalt being bound more firmly. The isotopic exchangeability studies further confirm this (Fig. 6.18). Over a period of 50 days, the isotopic exchangeability of sorbed cobalt fell from 35 per cent to almost zero. As there was little increase in the quantity of cobalt sorbed, this indicates that there was a change in the nature of

sorbed cobalt, over time, to a more firmly bound form.

The isotopically exchangeable cobalt was probably specifically sorbed cobalt held by the replacement of weakly dissociable hydrogen ions on the soil oxide surface. This form of sorbed cobalt would be particularly susceptible to desorption following an increase in the solution hydrogen ion concentration and a proportion of it would be desorbed by an increase in solution calcium concentration.

The non-isotopically exchangeable cobalt could be cobalt held by precipitation on the soil oxides or by replacement of the major metal ions in the oxide material.

The irreversibility of the reaction between cobalt and the manganese oxide birnessite was demonstrated by McKenzie (1967). He also showed that the extractability of sorbed cobalt by 2.5% acetic acid solution decreased with time.

It is of note that, in this study, the sorption of cobalt by impure soil birnessite was not affected by the presence of Mg^{2+} in solution (Table 6.2). This result is in contrast to cobalt sorption by montmorillonite, which was significantly reduced in the presence of Mg^{2+}. It was suggested that this was a result of magnesium competing with cobalt for entry into the clay mineral lattice.

The result with the birnessite material indicates that entry into spaces in the oxide structure was not an important mode of cobalt sorption.

Specific sorption of cobalt on oxides by exchange with bound hydrogen has been reported by Forbes et al. (1976) on goethite and Loganathan et al. (1977) on δ-MnO_2. It

was suggested above that the isotopically exchangeable sorbed cobalt was that form which had replaced bound hydrogen.

Benjamin and Leckie (1981), however, concluded that adsorption of cobalt, and other trace metals, onto amorphous iron oxyhydroxide, occurred at various types of site.

Loganathan et al. (1977) observed that there was some release of manganese with cobalt sorption onto δ-MnO_2 as well as replacement of disscciable hydrogen. McKenzie (1970) observed that on cobalt sorption onto manganese dioxide minerals, there was a release of structural manganese. He suggested that, following adsorption of cobalt on the oxides, diffusion into the mineral took place where the cobalt oxidised and replaced Mn^{3+}. This reaction is favoured by the fact that there would be a large gain in crystal field stabilisation energy from the formation of the low-spin Co^{3+} ion in an octahedral complex. X-ray photoelectron spectroscopy measurements of cobalt sorbed onto birnessite provided strong evidence that Co(II) had been oxidised to Co(III) (Murray and Dillard, 1979).

The replacement of structural manganese in δ-MnO_2 by cobalt (III) was proposed by Burns (1976), who suggested, again that the reaction was thermodynamically favourable as a result of the gain in crystal field stabilisation energy. It was also suggested that the stability of Co(III) in an octahedral complex was so high that it would be difficult to leach from the oxide using aqueous solutions.

The quantity of sorbed cobalt which was shown, in the present experiment, to be non-isotopically exchangeable, was probably comprised predominantly of cobalt which had replaced manganese or iron in the oxides. Although there is little experimental evidence in the literature for the replacement of iron in iron oxides by sorbed cobalt, it is conceivable that this also takes place. There would be a gain in energy, according to crystal-field theory, by the replacement of Fe(III), in an octahedral complex, by low-spin Co(III). However, the reduction of Fe(III) in the oxide by Co^{2+} in solution is less favourable energetically than the reduction of Mn(III).

No general conclusions can be drawn from the results of the cobalt sorption on the geologically-derived oxides as to whether manganese or iron oxides are better sorbents for cobalt. The crystalline character of these materials suggests that there was greater chemical stability in the structure. Thus, the replacement of either Fe or Mn by cobalt would be more difficult than in the more amorphous soil-derived oxides. The greater sorption of cobalt by manganite than by pyrolusite (Fig. 6.14) however, indicates that there may have been substitution of cobalt for manganese within the manganite. McKenzie (1970) proposed that cobalt replaced low valence manganese in the oxides which had previously substituted for Mn(IV). This latter substitution does not appear in pyrolusite, so that cobalt sorption by pyrolusite was lower than with other manganese oxide minerals.

The oxide derived from soil concretions showed a greater capability for cobalt sorption than soil birnessite. The former material contained greater amounts of both iron and manganese so, no conclusions can be drawn as to the relative importance of iron and manganese oxides in cobalt sorption in these materials.

It appears that cobalt specific sorption on soil oxide material takes place by two main reactions. Firstly, a high energy form of sorption which is probably caused by the replacement of the major metal cation within the oxides. This is more favourable energetically with manganese than iron. This substitution would predominate the cobalt sorption process at low surface coverage. Secondly, a low energy form of sorption which probably takes place by bonding of cobalt to structural surface oxygen atoms and hydroxyl groups in the oxides. This lower energy form of cobalt specific sorption would play a more important role in the total specific sorption as cobalt concentration, on the oxide increases.

6.3.3 SORPTION OF COBALT BY HUMIC AND FULVIC ACIDS

As discussed previously, with reference to the sorption of cobalt by intact soils, the rectilinear sorption isotherms obtained for humic and fulvic acids (Figs. 6.10, 6.15) indicate that only sorption at low site coverage was involved. In addition, the isotherms indicate a constant bonding energy for cobalt by the organic materials within the concentration range studied. In contrast, the sorption of

cobalt by montmorillonite and soil-derived oxides was shown to be at different energy levels and probably involved more than one type of sorption site.

Although the cobalt sorption behaviour, exhibited by humic and fulvic acids were similar the results were complicated by greater dispersion of the fulvic acid into solution. Nevertheless, the energy with which cobalt was sorbed by the two materials appears to be relatively similar.

At the solution calcium concentrations likely to be encountered in soil ($\sim$ 0.01M), almost all of the cobalt, in the humic acid system, was in the sorbed state (Figs. 6.2, 6.3). However, at higher solution calcium concentration, there was a decrease in the amount of cobalt sorbed. This could be attributed to increased flocculation of the humic acid and partly to the decrease in chemical activity of cobalt in solution.

There is no evidence, from the results, that calcium interfered directly with the specific sorption reaction between cobalt and the humic acid.

The desorption curve for cobalt sorbed on humic acid (Fig. 6.10) shows a lesser degree of hysteresis than the montmorillonite desorption curve (Fig. 6.9). It was previously proposed that the latter material sorbed cobalt, to some degree, by solid state entry of cobalt into the clay mineral crystal lattice. The trends of the desorption curves for humic acid suggest that there is little physical occlusion of cobalt sorbed by humic acid. This

theory is further supported by the extremely high isotopic exchangeability of cobalt sorbed on humic acid (Fig 6.17).

With decreasing solution pH, below a pH of 5.0, there was a large decrease in cobalt sorption by humic acid (Figs. 6.4, 6.5) which was possibly a result of direct competition from hydrogen ions for cobalt specific sorption sites on the humic acid.

Cobalt, along with other transition metals is commonly thought to form organo-metal complexes with humic and fulvic acids; the ligands being mainly carboxylic and phenolic groups (Stevenson and Ardakani, 1972). Schnitzer and Skinner (1967) observed a decrease in the stability constants of transition metal-fulvic acid complexes with a decrease in solution pH from pH 5.0 to 3.5. They attributed this to the greater ionisation of the carboxyl functional groups at the higher pH, causing more metal ions to be complexed.

It appears unlikely in the present experiment, because of the presence of excess solution calcium, that cobalt would be held at carboxylate functional groups by simple electrostatic force. Cobalt is probably held at acidic groups on the humic and fulvic acids by chelation processes. These sites may be carboxylic and phenolic groups which also function in cation exchange, but the high stability energy gained by complex formation with cobalt may cause the associated exchangeable cation (Ca^{2+}) to be displaced into solution. Also cobalt may form complexes with other functional groups having a high pKa value, including less acidic phenolic and carboxylic acid groups and alcoholic

groups. These groups would not be important in cation exchange, but could form complexes with cobalt and other transition metals.

The increase in solution hydrogen ion concentration may have had a direct effect on the specific sorption chelation reactions between cobalt and humic acid functional groups. Lehman (1963) maintained that hydrogen ions compete effectively for chelation by chelating agents, especially where the stability constant between the metal and ligand is small.

Although a large proportion of the sorbed cobalt remained exchangeable with cobalt in solution, there was a decrease in its isotopic exchangeability with time (Fig. 6.17). This would require the formation of complexes between cobalt and the organic ligands, which had higher stability constants.

It is of interest that the isotopic exchangeability of sorbed cobalt did not decrease continuously during the sorption period, as in montmorillonite and the soil concretion oxides, but reached a minimum after about 40 days.

6.3.4 SORPTION OF COBALT BY SOILS

The slopes of the cobalt sorption isotherms (Figs. 6.6, 6.7) were highly dependent on the soil pH. Thus, the log gradient (Table 6.1) and soil pH, measured in $CaCl_2$ solution, were correlated by a coefficient of 0.80 ($P < 0.001$). The results do not appear to show any relationship between the cobalt sorption characteristics of the soils and their contents of iron, manganese, clay or organic matter.

The cobalt sorption isotherms were rectilinear, implying that there was a large excess of sites available for the specific sorption of cobalt. At a larger range of cobalt concentrations then the isotherms would become curvilinear. The sorption capacities of the soils for cobalt could not be calculated, but it is likely that the solid phase composition of the soils would influence their capacity for cobalt sorption.

At the low cobalt concentrations studied, it is evident that the equilibrium between solution phase cobalt and cobalt in the solid phase of the soil is largely dependent on the soil pH.

Tiller et al. (1969) studied the specific sorption of cobalt on five different soil groups from Australia. Their results showed that, within each soil group, the gradient of the sorption isotherm was directly related to soil pH.

In order to compare the abilities of both intact soils and constituents of soils to sorb cobalt, the slopes of their cobalt sorption isotherms are presented in Table 6.4. In the cases of montmorillonite, soil concretion oxides and birnessite, the gradients of the isotherms at low cobalt surface coverage are used.

Table 6.4. Cobalt sorption isotherm gradients for intact soils and soil constituents.

Sorbent	pH of sorption	Isotherm grad($^{ml}/_{g}$)	Soln Co concn ($\mu g/ml$)
Soils	5.0-5.7 6.0 6.1-6.6	42.6-209 324 489-1986	0.004-0.052 0.001-0.003 0.0-0.008
Montmorillonite	6.2	371	0.0-0.100
Kaolinite	6.1	5.1	0.0-0.076
Illite	6.4	50.1	0.0-0.315
Concretion oxide	6.0	33,884	0.0-0.066
Pure birnessite	6.4	7,943	0.0-0.022
Humic acid	6.0	1,738	0.0-0.053
Fulvic acid	6.0	912	0.0-0.098

The concentration ranges of cobalt studied for the soil constituents were, in general, similar in magnitude to those for the intact soils.

The soils used in this study were from South-East Scotland and the clay minerals likely to be present in greatest concentration are kaolinite and illite. Significant amounts of montmorillonite are unlikely to be present (Ragg, 1960; Ragg and Futty, 1967).

The average clay content of the soils was 20 per cent. If the cobalt sorption by the soils was attributable solely to the kaolinite and illite within them, then the isotherms for the soils would range from about 1 ml/g to 10 ml/g. These values are much smaller than those actually obtained, even at low soil pH. It therefore appears that the clay mineral fraction is of limited importance in cobalt sorption by these soils.

The humic and fulvic acids exhibited a greater ability to sorb cobalt than the clay minerals. The average concentration of organic matter in the soils was 5.4 per cent. If it is assumed that the organic matter was responsible for cobalt sorption in the soils and that it can sorb cobalt to the same extent as humic acid, the cobalt sorption isotherm for a soil at pH 6.0 would have a gradient of about 94 ml/g. This is compared to the gradient of 324 ml/g actually obtained experimentally for a soil at pH 6.0. However, it is highly unlikely that the soil organic matter would have as great a capability for cobalt sorption as the humic acid due to the smaller concentration of functional groups, on the organic matter, able to sorb cobalt.

It therefore seems probable that the soil oxide fraction is mainly responsible for cobalt sorption in the soil samples.

In trying to determine which component (ie iron or manganese) of the soil oxides is of more importance in cobalt sorption by soils, the results of the cobalt sorption by the concretion oxides and birnessite can be used. If it is assumed that the sorption of cobalt by these two soil constituents was by the iron oxide fraction then the sorption gradients per gram of iron are $2{\cdot}6 \times 10^5$ ml/g for the soil concretion oxides and $4{\cdot}2 \times 10^5$ ml/g for the soil-derived birnessite. The average content of iron in the soils was 2.04 per cent and, if this fraction was wholly responsible

for cobalt sorption, then the isotherm would have a gradient of 5,237 ml/g or 8,528 ml/g, the values being calculated from the iron contents of the soil concretion oxides and birnessite respectively. These values are far in excess to the sorption gradient obtained for a soil at pH 6.0.

If the assumption is made that in the two oxide samples the manganese oxides alone cause cobalt sorption, then the sorption gradients per gram of manganese are $5{\cdot}8 \times 10^5$ ml/g for soil concretion oxides and $2{\cdot}6 \times 10^5$ ml/g for birnessite. In the soils the average manganese content was 356 ppm Mn and if cobalt sorption was attributable solely to the manganese oxide fraction the sorption isotherm would have gradient 208 ml/g (calculated from manganese content of concretion oxides) or 94 ml/g (calculated from the manganese content of soil birnessite). These calculated values show a similarity to those obtained experimentally for a soil at pH 6.0.

These results suggest that manganese oxides play a proportionately greater role than iron oxides in cobalt sorption in the soils studied.

Tiller et al. (1969) studied cobalt sorption by Australian soils at a higher surface coverage than in the present experiment. They obtained curvilinear isotherms and were able to calculate the sorption capacity of the soils for cobalt. The Langmuir sorption capacities for the soils were highly correlated with the soil manganese content.

The irreversible sorption of cobalt by the replacement of iron or manganese within their respective oxides is thermodynamically more favourable with manganese than iron. It should be noted, however, that the concentration of iron is approximately 70 times that of manganese. Therefore, the surface available for the initial sorption of solution cobalt will be comprised predominantly of iron oxide (and aluminium oxide). Over time cobalt would be irreversibly sorbed by the manganese oxides. Means et al. (1978b) investigated the fate of cobalt-60 from radionucleide waste burial trenches and found it to become associated mainly with the manganese oxides. There was a lack of correlation between soil-extracted cobalt-60 and amorphous iron oxide content. However, the soils were sampled and analysed at least 8 years after the last waste material had been buried.

In contrast to this, Abd-Elfattah and Wada (1981) found that the concentration of iron oxide in soil had the greatest effect on the selective adsorption of several metals, including cobalt. This was in comparison to other cation exchange materials such as halloysite, humus, allophane and montmorillonite. However the manganese oxide content was not considered.

It would seem likely that the initial sorption of cobalt takes place to a large extent by the soil iron oxides before its irreversible sorption by the manganese oxides. This process would be speeded up in the sorption of cobalt carried

out in laboratory conditions. The higher solution to soil ratio and the continual agitation of the solid and solution phases would cause the rate at which cobalt is desorbed from iron oxides and irreversibly sorbed by the manganese oxides to be increased.

6.4 Conclusions

The concentrations of solution cobalt used in these studies were likely to be similar to those present in the soil solution. Thus the results of these studies should be relevant to the behaviour of cobalt in soil.

It is evident that the clay mineral fraction of most soils is unlikely to play a significant role in determining the behaviour of soil cobalt. However, where soils have a high montmorillonite content, as for instance some tropical soils, then a substantial proportion of the soil cobalt may be held in the clay mineral fraction.

Soil organic-matter is only likely to play a major role in cobalt sorption where pasture has been top-dressed. Cobalt, which would be in relatively high concentration at the soil surface, could be held by both cation exchange and specific sorption. However, as was indicated by the results of the isotopic exchange studies, the ability of humic acid to 'fix' added cobalt is small and after time, through desorption of the chelated cobalt, it would be released back into the soil solution. The importance of soil organic matter in holding native soil cobalt is probably very small.

It was shown that the soil oxides play the major role in the sorption of cobalt. The high energy with which sorption takes place and the ability to 'fix' sorbed cobalt indicates that the soil

oxides would eventually provide a 'sink' for cobalt added to soils. Most of the cobalt bound by these oxides at normal pH levels would become irreversibly sorbed and unavailable to plant uptake. Entry of 'fixed' cobalt back into solution could only be achieved by dissolution of the soil oxide at low solution pH, or by the presence of reducing conditions in the soil.

The results indicated that the soil manganese oxides play a proportionately greater role in cobalt sorption than the iron oxides.

CHAPTER 7.

THE UPTAKE OF NATIVE COBALT BY PERENNIAL RYE GRASS AND RED CLOVER FROM SOILS OF SOUTH-EAST SCOTLAND UNDER GLASSHOUSE CONDITIONS.

In comparison to published work on the plant uptake of trace metals such as copper, zinc and manganese from soils, only a few studies have concentrated on measuring the ability of soils to supply plant-available cobalt. Pot experiments were carried out by Nicholls and Honeysett (1964a) to assess the availability of cobalt to subterranean clover in over 100 surface soils in Tasmania. Other workers have used pot trials to study the effects of soil moisture status on the uptake of native soil cobalt by plants. (Adams and Honeysett, 1964; Kubota et al. 1963).

The extent of soil cobalt uptake by plants has been examined in relation to other measured soil parameters such as the concentration of isotopically exchangeable cobalt, (Graham, 1973; Gille and Graham, 1971; Lopez and Graham, 1972) and cobalt extracted by chemical reagents (Gille and Graham, 1971; Reddy and Mehta, 1961).

Although the results of pot trials in glasshouse conditions may not be wholly applicable to the field situation, the greater control of soil and plant growth conditions increases the possibility of being able to assess which soil factors influence plant uptake of cobalt. In soil cobalt experiments it is particularly important to be able to control and monitor the moisture status of the soils, and this is done more easily under glasshouse conditions. The pot trial is also advantageous in that the risk of soil contamination during herbage sampling is lessened.

The present experiment was designed to measure the uptake of native soil cobalt by perennial ryegrass and red clover from surface soils of the Lothians and Borders regions of Scotland. These soils were from a number of soil series, some of which tend to be deficient in plant-available cobalt.

It was proposed to examine the plant uptake of cobalt in relation to the following soil factors:-

(a) intrinsic soil properties such as pH, cation exchange capacity, clay content and organic matter content.

(b) total soil cobalt and cobalt extractable by acetic acid, E.D.T.A. and calcium chloride.

(c) isotopically exchangeable cobalt.

(d) cobalt sorption properties of the soils.

7.1 Experimental Method

7.1.1 SOILS

The collection and subsequent treatment of the soil samples is described in section 4.1.1. The chemical and physical analyses of the soils are described in section 2.1.

7.1.2 EXTRACTABLE AND ISOTOPICALLY EXCHANGEABLE COBALT

The extracting solutions used are described in section 4.1.2 and the methods of cobalt extraction described in sections 2.2.1, 2.2.2 and 2.2.4.

Isotopically exchangeable cobalt measurement is described in section 2.2.3.

7.1.3 SORPTION OF COBALT BY SOIL

The cobalt sorption isotherms for the soils were obtained by the method described in section 6.1.2.

7.1.4 THE POT EXPERIMENT

Standardisation of soil moisture tension

Moist samples of each of the 20 soils, weighing approximately 2.5 kg, were placed in plastic pots. Tensiometers were inserted into the soils and the soils repeatedly wetted and allowed to dry. The pots were re-weighed at the required moisture tension of 1×10^4 Pascals (= 7.5 cm Hg). Thus the volumes of water required to be added to (or lost from) the soils in their original moist state to attain the standard moisture tension, were obtained.

The soils, at this standard moisture tension, contained readily-available water for plant growth but were at a moisture tension below field capacity.

Growth of ryegrass and clover

Six 2.5 kg samples of each of the soils were weighed into plastic pots. In each of 3 replicate pots approximately 40 red clover seeds (Trifolium pratense L. var. Grassland Huia) were sown, and in each of the other 3 replicates approximately 110 seeds of perennial ryegrass (Lolium perenne L.var. S23) were sown.

Fertiliser was applied to each soil in deionised water solution so that each pot received 228 mgs NH_4NO_3, 70 mgs KH_2PO_4 and 20 mgs K_2SO_4. This was equivalent to an addition of 40 ppm N, 8 ppm P and 16 ppm K to air-dry soil.

The tops of the pots were covered with polythene sheeting and shaded from sunlight until germination of the seeds had taken place. The pots were then arranged randomly within 3 blocks in the greenhouse.

The pots and soils were weighed and the correct volume of deionised water added to each pot to achieve a standard moisture tension of 1×10^4 Pascals. Where necessary, the soils were allowed to dry to achieve this moisture tension. The pots and soils were thereafter periodically weighed, at about 3-day intervals, and the required volumes of deionised water added. The plants were weeded when necessary.

Approximately 60 days after seed germination, the herbage from the pots was harvested, using stainless steel scissors, weighed and dried at $110^{\circ}C$.

The herbage samples were analysed for cobalt content as described in section 2.3. In the clover samples, only one replicate per pot was analysed. At least 2 replicates per pot were analysed from the ryegrass samples.

7.2 Results and Discussion

7.2.1 SOILS

Some of the physical and chemical properties of the 20 soils are presented in Table 4.1 of the Results and Discussion section of Chapter 4. Extractable soil cobalt and isotopically exchangeable cobalt contents of the soils are presented in Tables 4.3 and 4.5, respectively of Chapter 4.

7.2.2 PLANT UPTAKE OF SOIL COBALT

The average weights of herbage dry matter obtained from each soil, and the concentrations of cobalt in the herbage dry matter are presented in Table 7.1.

Where no values are presented for the clover cobalt concentration the yield was too small to obtain an adequate quantity of herbage dry matter for cobalt analysis.

Table 7.1. Herbage dry matter yields and cobalt concentrations. (Mean of 3 replicate samples).

SOIL NO	Wt. D.M. ryegrass (g)	Co concn in ryegrass (μg/g)	Wt. D.M. clover (g)	Co concn in clover (μg/g)
1	5.0	0.06	-	-
2	9.3	0.07	5.6	0.06
3	8.3	0.19	3.8	0.21
4	10.8	0.08	7.8	0.10
5	9.5	0.13	5.9	0.16
6	9.2	0.07	9.2	0.05
7	5.7	0.07	3.7	0.06
8	3.3	0.23	-	-
9	7.0	0.14	4.0	0.19
10	6.4	0.08	5.0	0.05
11	7.3	0.09	5.0	0.09
12	7.9	0.06	4.6	0.05
13	4.7	0.07	-	-
14	4.5	0.10	-	-
15	7.8	0.14	2.5	0.09
16	5.6	0.96	-	-
17	5.6	0.08	5.2	0.15
18	3.8	0.14	-	-
19	6.2	0.09	5.0	0.19
20	4.7	0.20	-	-

Although there was variation in the weight of dry matter harvested from different soils, it appears to have had little effect on the concentration of cobalt measured in the herbage.

The herbage cobalt concentration and dry matter yield were not significantly correlated in either the ryegrass or red clover.

There was a range in ryegrass cobalt concentration of 0.06 μg/g DM to 0.96 μg/g DM and 9 of the soils carried grass with levels of cobalt normally deficient for ovine nutrition, ie below 0.08 μg Co/g DM.

In a number of soils the concentration of cobalt was lower in the clover than the ryegrass. It has been shown, in some investigations, that clover species contain a greater concentration of cobalt than grass species growing on the same soil (Mitchell et al. 1957; Andrews, 1966). However, Andrews (1966) stated that there was negligible differences between the concentrations of cobalt in grass and leguminous species when growing on cobalt-deficient soils. The results of this pot experiment indicate that, where clover cobalt concentration was below that of ryegrass, both concentrations were deficient.

7.2.3 PLANT UPTAKE OF COBALT IN RELATION TO SOIL PROPERTIES

Table 7.2 presents the correlation coefficients for correlations between plant cobalt concentrations and some individual soil properties.

Table 7.2. Correlation coefficients between plant Co concentration and soil properties.

	$pH_{(H_2O)}$	% clay	% org C	CEC	% Mn	% Fe	Total Co
Concn. Co in ryegrass	xx -0.66	-0.23	x 0.53	0.20	-0.34	-0.35	-0.37
Concn. Co in clover	x -0.63	-0.29	0.31	0.39	0.20	0.12	0.03

xx $P < 0.01$
x $P < 0.02$

Clover and ryegrass cobalt concentrations were closely related and so although the following discussion pertains mainly to ryegrass cobalt contents, it is also relevant to clover.

Soil pH had a large influence on the uptake of cobalt by the plant material. This can be seen from Fig. 7.1 for both ryegrass and clover. A negative relationship between plant cobalt content and soil pH has been demonstrated both in field and glasshouse pot experiments (Reith and Mitchell, 1964; Beeson et al. 1948; Singh and Singh, 1966; Graham, 1973; Mokragnatz and Filipovic, 1961; Coppenet et al. 1972). However, Nicholls and Honeysett (1964a) and Reddy and Mehta (1961) obtained no relationship between soil pH and the plant assimilation of soil cobalt.

In the present experiment, it can be seen from Fig. 7.1, that below a soil pH of 6.4, the herbage cobalt tended to increase with a decrease in pH. Above pH 6.4 any change in soil pH did not appear to affect plant cobalt content. Soil 16

which had a pH, in water, of 5.1, had an exceptionally high ryegrass cobalt content of 0.96 µg/g D.M. It is of note that this soil had a very low total cobalt content of around 4 ppm, whereas many of the soils supporting cobalt deficient herbage had total cobalt contents above 10 ppm. It is not unexpected, therefore that, in general, the level of cobalt in the herbage was not significantly related to the total cobalt content of the soil, as measured by nitric/perchloric acid soil digest. This is a consequence of the fact that only an extremely small fraction of the total soil cobalt was taken up by the herbage; ranging from 0.000014 to 0.00069 per cent. Therefore the total cobalt content of the soil is unlikely to indicate the amount which is actually plant-available.

It is possible that the plant root obtains cobalt almost exclusively from the small concentrations present in soil solution and cation exchange sites of the clay minerals and organic matter. There was, however, no significant correlation between plant cobalt concentration and soil cation exchange capacity, but as there would be only a very small quantity of cobalt present on the cation exchange sites, the size of the soil's exchange capacity would have little influence on the actual amount present. This would be affected, to a greater extent, by variation in soil pH and the concentrations of other cations present in solution.

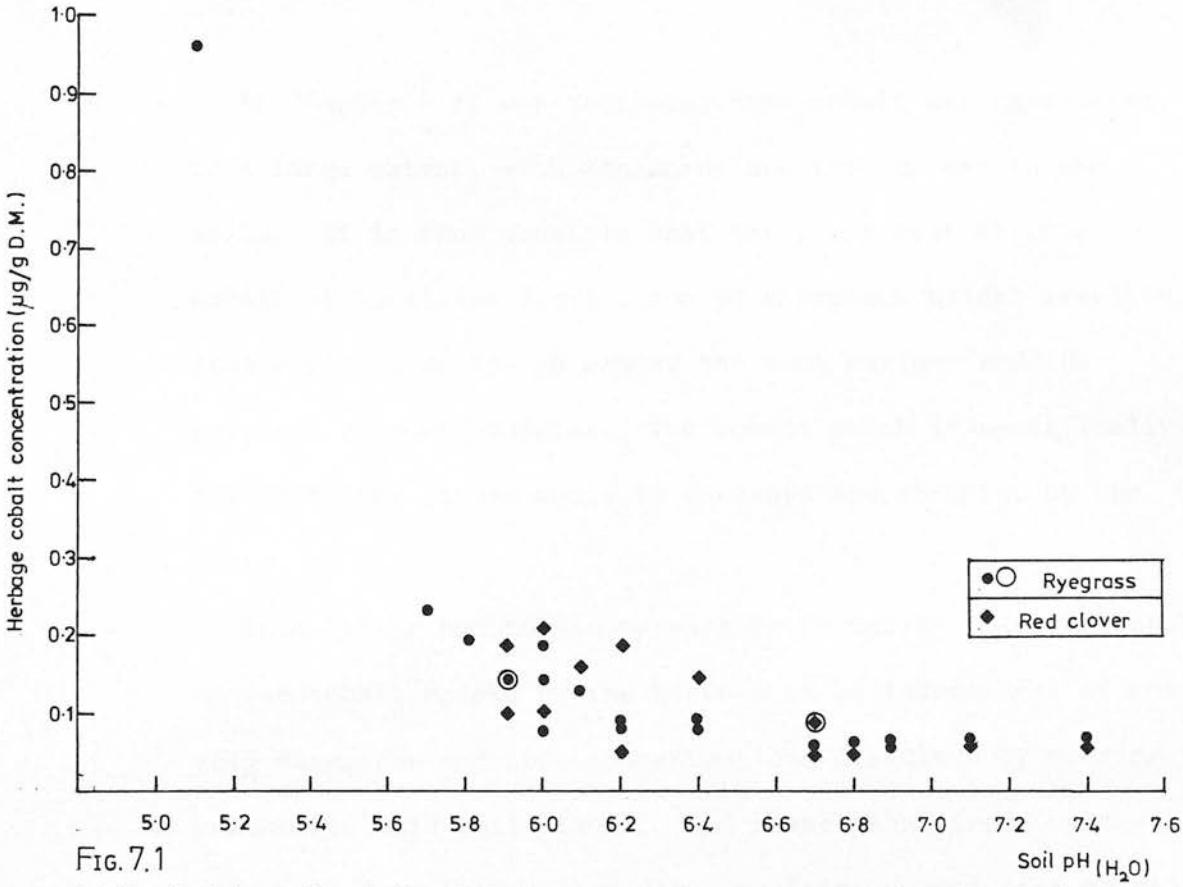


FIG. 7.1

Relationship between the cobalt content of ryegrass and red clover grown in pots and soil pH.

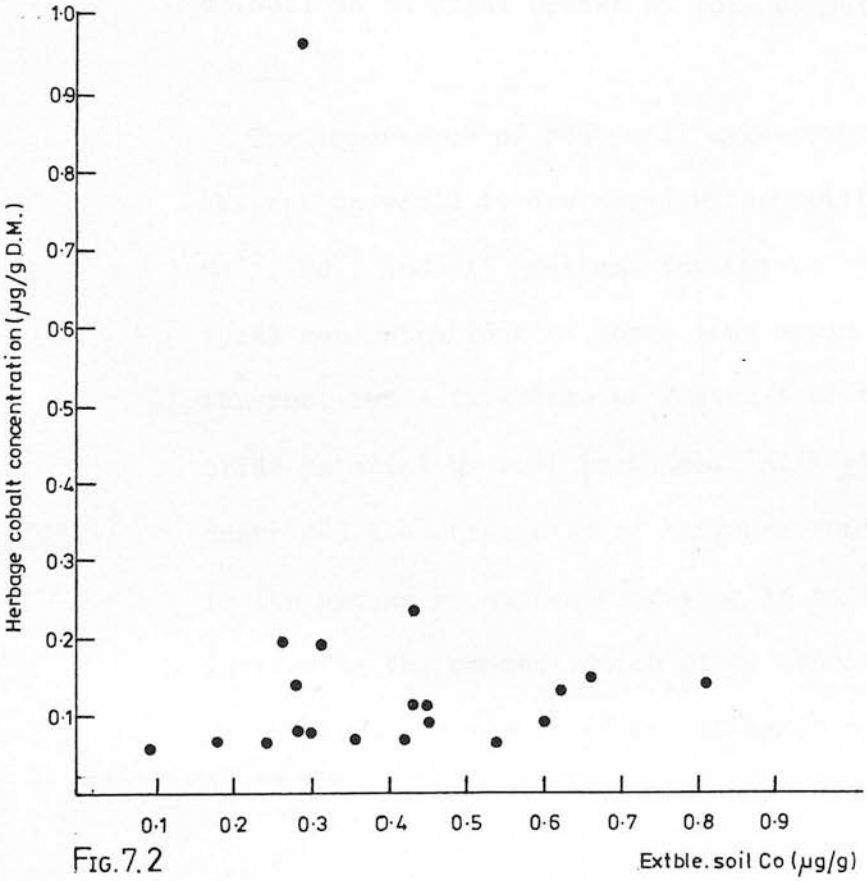


FIG. 7.2

Relationship between the cobalt content of ryegrass grown in pots and the concentration of soil cobalt extractable by 0·5M acetic acid.

In Chapter 4 it was concluded that cobalt was associated, to a large extent, with manganese and iron oxides in the soils. It is thus possible that the plant root absorbs cobalt by localised dissolution of amorphous oxides resulting from a region of low pH around the root surface and the presence of root exudates. The cobalt which is specifically sorbed by the oxides would be released and absorbed by the root.

This latter hypothesis appears to be unlikely as the results showed cobalt uptake by the herbage to be independent of the soil manganese and iron concentrations dissolved by nitric/perchloric acid soil digest. Had there been direct uptake of cobalt from the soil oxides a positive correlation between plant cobalt concentration and soil iron and manganese contents would have been expected. Also the important effect of soil pH on plant uptake of soil cobalt would not have been found.

The importance of root-soil oxide contact in cobalt absorption would be decreased by competition from Mn^{2+}, Fe^{2+} and Al^{3+} cations for uptake by the root. The local concentrations of these ions would be extremely high at the root-oxide interface as a result of the dissolution of oxide material by root exudates. Hill et al. (1953) described the antagonism of manganese and iron towards cobalt in its uptake by soybeans growing in nutrient solution. By increasing the concentration of manganese in solution from 0 to 1 ppm, the amount of cobalt taken up, from a solution

concentration of 0.02 ppm decreased by about two-thirds. Iron also significantly reduced plant cobalt uptake, but its effect was not so marked.

Ryegrass cobalt concentration showed a positive correlation with the organic carbon content of the soils (Table 7.2). Thus cobalt on the organic matter exchange sites and specifically sorbed by organic matter may have been an important source of cobalt to the ryegrass. However, the concentration of cobalt on the organic matter cation exchange sites is likely to be small because of competition from other ions in soil solution such as Ca^{2+} and Mg^{2+}. There will also be competition for the specific sorption sites by other trace metal ions in solution such as Fe^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+}. The total amount of cobalt held by the organic matter is thus likely to be very small.

The correlation between ryegrass cobalt concentration and soil organic carbon content was probably a result of the fact that, in general, soils with a high organic matter content had a low pH.

7.2.4 PLANT UPTAKE OF COBALT IN RELATION TO EXTRACTABLE SOIL COBALT

The concentrations of soil cobalt extracted by 0.5 M acetic acid solution, 0.04 M di-sodium EDTA solution and 0.05 M $CaCl_2$ solution for the 20 soils are presented in Table 4.3 of Chapter 4. The correlation coefficients for the relationships between herbage concentrations of cobalt and the concentrations of extractable soil cobalt are presented in Table 7.3.

Table 7.3. Correlation coefficients between plant cobalt concentration and extractable soil cobalt.

	Acetic acid Co	EDTA Co	$CaCl_2$ Co
Co concn. in ryegrass	-0.09	-0.22	xx 0.61
Co concn. in clover	-0.16	0.43	xx 0.78

xx $P < 0.01$

The only soil cobalt extractant which gave any indication of the quantity of plant-available cobalt in the soil was 0.05 M $CaCl_2$. It was suggested in Chapter 4, that calcium chloride extracted cobalt mainly from soil solution and it was shown that the concentration of cobalt extracted was indirectly related to soil pH. The cobalt in solution appeared to be derived from the specifically sorbed cobalt on the oxide fraction and the equilibrium between this sorbed cobalt and solution cobalt was pH dependent. At low soil pH a greater concentration of sorbed cobalt would move into solution and thus be extractable by calcium chloride.

Plant cobalt concentration would thus appear to be related predominantly to the concentration of cobalt in soil solution. In some soils exchangeable cobalt may also be of some importance in supplying plant-available cobalt.

Calcium chloride at 0.05 M concentration would not be able to displace a significant proportion of specifically sorbed cobalt on the oxide material. This was shown to be the case in Chapter 6, where only at calcium chloride solution concentrations of 0.5 M were significant proportions of specifically sorbed cobalt desorbed into solution from soil oxide material.

Both 0.5 M acetic acid and 0.04 M di-sodium EDTA are likely to have extracted cobalt specifically sorbed by soil oxides along with cobalt which is an integral part of the oxide structure. From the significant relationship between cobalt extracted by these two extractants and total soil cobalt (Chapter 4, Table 4.4) it is not unexpected that they were inadequate in assessing the concentration of plant-available cobalt in the soils (Table 7.3). However, Mitchell et al. (1957) reported a highly significant correlation between mixed herbage, ryegrass and clover cobalt contents against the concentrations of soil cobalt extracted by acetic acid and EDTA. Lakanen and Ervio (1971) suggested, from the results of a pot experiment using oats, that acid ammonium acetate/0.02 M EDTA was a suitable soil extractant for trace metals.

In the 20 soils of the present experiment, acetic acid extracted 2 to 7 per cent, and EDTA 3 to 20 per cent of the total soil cobalt. The mean values were 4 and 12 per cent respectively, which are far in excess of the proportions likely to be plant-available in the soil.

Figure 7.2 further exhibits the lack of association between ryegrass cobalt concentration and acetic acid extractable soil cobalt. It can be seen that in at least 7 of the soils, the extractable soil cobalt levels appeared to be sufficient (>0.25 µg/g) whereas the plant concentrations were around the deficient level of 0.08 µg/g D.M.

Although neither extractant, on its own, gave an adequate indication of plant-available cobalt, by considering extractable soil cobalt in combination with soil pH a relationship with plant cobalt level was apparent. This is shown in Figure 7.3 for acetic acid extractable soil cobalt. EDTA-extractable soil cobalt did not give such a clear differentiation between herbage which was sufficient and herbage which was deficient in cobalt.

Figure 7.3 shows that a soil with a pH value of 6.0 and an acetic acid extractable cobalt concentration of 0.3 ppm will produce herbage just adequate in cobalt for grazing livestock. However, if the soil had a pH of 6.5 then the herbage would be deficient in cobalt. Soils with a pH above 6.8 are likely to support cobalt-deficient herbage, regardless of the extractable cobalt content.

Thus acetic acid appears to extract cobalt which is potentially plant-available, but its actual availability appears to be dependent on soil pH.

7.2.5 PLANT UPTAKE OF SOIL COBALT IN RELATION TO ISOTOPICALLY EXCHANGEABLE COBALT

The values for isotopically exchangeable cobalt on the soil solid phase are presented in Chapter 4, Table 4.5 and isotopically exchangeable cobalt, in both solid and solution phases, in Chapter 4, Table 4.7.

The most likely source of the solid phase isotopically exchangeable cobalt is specifically sorbed cobalt and it might be expected that this would be a major source of plant available

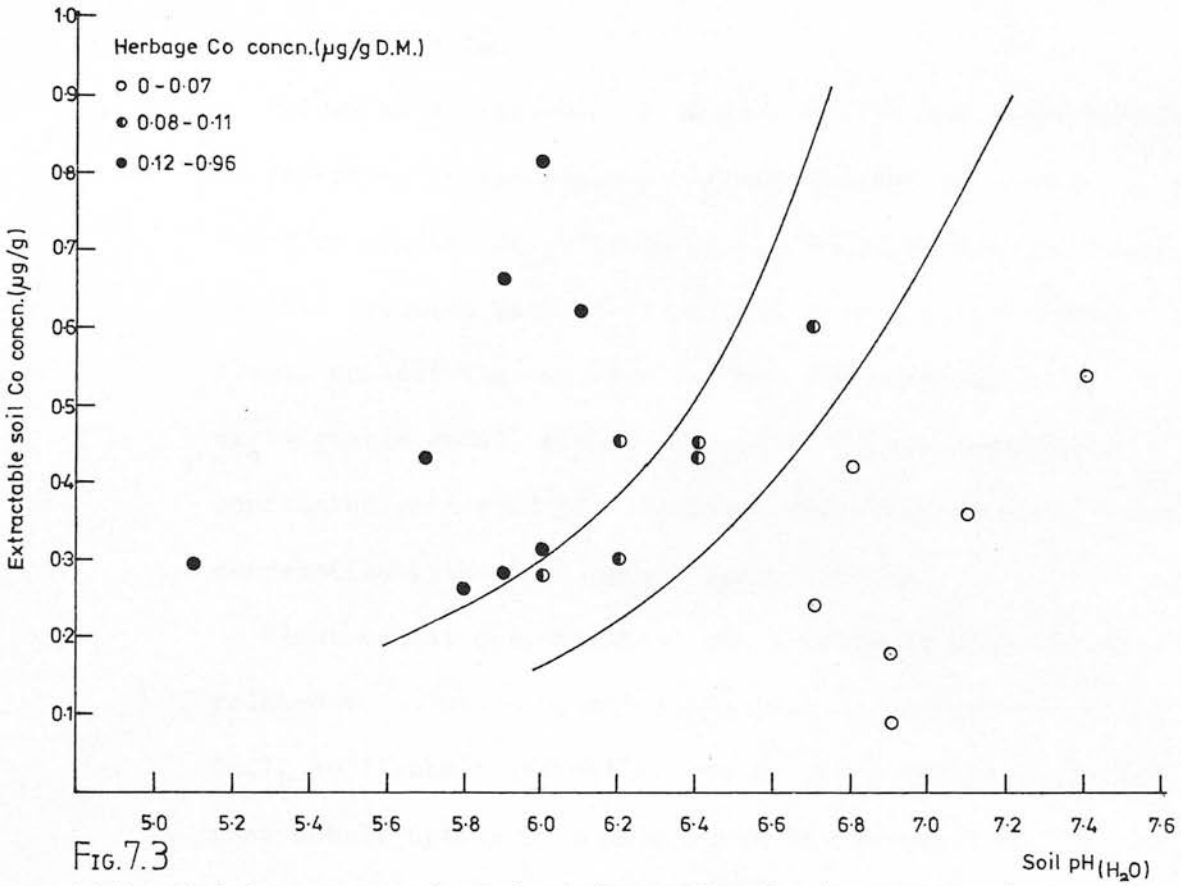


FIG. 7.3

Cobalt content of ryegrass grown in pots in relation to 0 5M acetic acid - extractable soil cobalt and soil pH.

cobalt. However, there was no correlation between solid phase isotopically exchangeable cobalt levels and plant cobalt concentration. The former values were significantly correlated with the total soil cobalt content and manganese and iron contents.

Values were obtained, in Chapter 4, for the concentrations of isotopically exchangeable cobalt present in both solid and solution phases (Co_{ie} (total)). The concentration of cobalt in this fraction was less dependent on the soil's total cobalt content than was the surface phase isotopically exchangeable cobalt alone. Co_{ie} (total) was negatively correlated with soil pH. However, there was no significant correlation with plant cobalt concentration.

Plant cobalt concentration was previously shown to be related to solution cobalt concentration as measured by $CaCl_2$ soil cobalt extraction and it could thus be expected that cobalt uptake by plants would be dependent on the equilibrium between solid phase and solution phase isotopically exchangeable cobalt. As was shown in Chapter 4, this can be measured by the ratio Co_{ie} (sorbed): Co_{ie} (total).

Ryegrass cobalt concentration was negatively correlated to this ratio ($r = -0.75$, $P < 0.001$) which is not unexpected since this ratio was shown, in Chapter 4, to be directly correlated with soil pH.

For the soils in this study the ratio was independent of the actual concentration of cobalt present in the soil system.

7.2.6 PLANT UPTAKE OF SOIL COBALT IN RELATION TO SOIL COBALT SORPTION CAPACITY

In Chapter 6 a study was made of the specific sorption of cobalt onto 18 of the soils used in the present experiment. The sorption isotherms for cobalt are presented in Figs. 6.6 and 6.7 of that chapter and the gradients of the isotherms presented in Table 6.1.

There was a highly significant positive correlation between the log of the isotherm gradient and soil pH and it is therefore not unexpected that there was an indirect relationship between the former quantity and the log of ryegrass cobalt concentration ($r = 0.61$, $P < 0.01$).

In Chapter 6 it was concluded that sorption of cobalt in soil was taking place predominantly on the soil oxide fraction and it has been suggested previously that plant-available cobalt is derived from specifically sorbed cobalt on the soil oxides.

The availability of cobalt to the plant root would depend on the net concentration of cobalt which desorbs from the solid phase whereas the sorption of cobalt, as measured by the sorption isotherms, will depend on the net concentration of added cobalt which sorbs onto the solid phase. Both of these quantities are thus dependent on the equilibrium state of the sorption-desorption reaction between cobalt and the soil solid phase. The equilibrium state is dependent on soil pH. Thus the soil cobalt sorption characteristics and plant uptake of cobalt from soil are inter-related.

7.3 Conclusions

Fewer than half of the soils in this experiment produced herbage containing sufficient cobalt for ovine nutrition. Thus the results of the experiment are relevant mainly to soils of low plant-available cobalt content. Of the soil properties determined only soil pH appeared to have a significant effect on plant cobalt concentration. Had a wider range of soils been used, from a more variable geological background, other relationships between soil properties and plant cobalt levels might have emerged.

In the field situation the effect of soil pH on cobalt uptake could be masked by other variables such as a high variation in amorphous oxide levels. Variability in soil moisture content is also likely to influence the levels of plant-available soil cobalt, as was concluded in Chapter 5.

The results for plant uptake of cobalt demonstrated that when cobalt concentration in ryegrass was deficient for animal nutrition it was also deficient in red clover. Thus increasing the percentage of clover in a pasture sward growing on a cobalt-deficient soil may not necessarily increase the pasture content of cobalt.

In the reclamation of hill land, previously used for rough grazing, it is often the policy to introduce white clover into the pasture sward. In order to do this the soil pH may have to be increased to above 6.0, by application of lime for optimum growth of the clover. The raising of the pH may cause the plant-available cobalt concentration in the soil to decrease sharply, leading to pasture herbage which is deficient in cobalt. In situations where the potentially plant-available soil cobalt appears

to be low, it may be more prudent to sow grass species, which are more tolerant of low pH, and allow the soil pH to remain below 6.0. Alternatively, cobalt could be applied to the soil by top-dressing, or livestock could be dosed with cobalt.

The pot experiment revealed that there was a very limited uptake of native soil cobalt by the herbage. Assuming a yield of 8,000 kg D.M./ha/yr of pasture herbage on average 0.003 per cent of the total cobalt in the top 20 cms of soil would be removed each year by the pasture herbage. The cobalt uptake over one year would be equivalent to only 0.2 per cent of the isotopically exchangeable soil cobalt. In soils of low pH, where plant assimilation of cobalt was greater, then the equivalent proportion could rise to 3 per cent. However, because at low soil pH there is greater dissolution of soil oxides the isotopically exchangeable cobalt fraction would be quickly replenished from cobalt fixed within the oxides.

The concentration of soil cobalt extractable by 0.05 M $CaCl_2$ was a superior indicator of the concentration of plant-available cobalt to the concentration extracted by either 0.04 M di-sodium EDTA or 0.5 M acetic acid solution. The concentration extracted by calcium chloride was highly dependent on soil pH whereas that extracted by the latter two extractants was more dependent on the total cobalt content of the soil.

Difficulties may arise in the use of calcium chloride as an extractant for soil cobalt in that only a small quantity of cobalt is extracted for analysis. Methods used in the routine analysis of soils for plant-available cobalt may not be sensitive enough for the detection of this quantity. If this is indeed the case then, as

was shown in the results, acetic acid extractable soil cobalt may give an adequate estimation of the plant-availability of soil cobalt if soil pH is taken into account.

The results indicate that the plant root absorbs cobalt from soil solution and that this solution cobalt is derived from cobalt specifically sorbed on the soil oxides. The percentage of this cobalt which enters into solution increases with decreasing pH and consequently plant cobalt content increases with decreasing soil pH.

CHAPTER 8.

THE UPTAKE OF SUPPLEMENTARY COBALT BY PERENNIAL RYEGRASS FROM SOILS OF SOUTH-EAST SCOTLAND UNDER GLASSHOUSE CONDITIONS

Since the diagnosis of cobalt deficiency in livestock in New Zealand and Australia during the 1930s, a number of field experiments have been carried out to monitor the change in pasture cobalt content on soils which have been top-dressed with cobalt salts. These include the work of Askew and Dixon (1937) in New Zealand, Adams *et al.* (1969), Rossiter *et al.* (1948) in Australia, Percival *et al.* (1955) in the U.S.A., Mitchell *et al.* (1957), Reith and Mitchell (1964), Stewart *et al.* (1941, 1942, 1946) and McLaren *et al.* (1979) in Scotland.

Glasshouse pot experiments have also been utilised in assessing the plant uptake of soil applied cobalt in more regulated conditions. Nicholls and Honeysett (1964b) measured the uptake of applied cobalt by subterranean clover, perennial ryegrass and white clover from 27 Australian soils. Adams *et al.* (1969), also in Australia, used both field and pot experiments in order to investigate soil characteristics which influence the effectiveness of cobalt application. The cobalt levels of the untreated soils ranged from those in which cobalt deficiency was unlikely, to those in which cobalt deficiency was common. The uptake of applied cobalt by pasture plant species was compared with laboratory measurements on the cobalt adsorption behaviour of the soils.

McLaren and Williams (1981) measured the assimilation of cobalt by red clover and perennial ryegrass from both cobalt sulphate and cobalt-EDTA applied to the soil.

The object of the present experiment was to monitor the uptake by perennial ryegrass of cobalt applied to soils of south-east Scotland, most of which were low in plant-available cobalt. These same soils were used in the experiment to investigate the plant uptake of native cobalt as described in Chapter 7.

Because of the large effect of soil moisture on the available cobalt content of soils, it was necessary to maintain the soils at a constant moisture tension.

A comparison was made between uptake of cobalt by herbage on soils to which cobalt was applied as the sulphate salt and as the EDTA complex. The plant availability of the applied cobalt was examined in relation to various properties and parameters; including extractable soil cobalt, the cobalt sorption characteristics of the soils and the isotopic exchangeability of cobalt.

The cobalt treatments were designed to add around 0.5 µg/g cobalt to the top 20 cm of soil which is equivalent to the quantity currently recommended by the East of Scotland College of Agriculture for pasture top-dressing (6 kg $CoSO_4.7H_2O$ per ha.).

8.1 Experimental Method.

8.1.1 SOILS

Twelve soils were used. These were also used in the pot experiment to study the plant uptake of native cobalt. The methods of sampling, treatment and analyses are described in section 4.1.

8.1.2 THE POT EXPERIMENT

A volume of $CoSO_4.7H_2O$ solution, between 200 to 250 ml, was added to 3.7 kg of moist soil in a polypropylene bucket. The addition was designed to add 0.50 µg/g of cobalt to air dry soil, and thus the volume of the solution added was adjusted to

account for the moisture content of the soils.

The Co-EDTA additions were made to only 5 of the soils. These were made in volumes of around 75 ml of solution to 3.7 kg moist soil. The addition was designed to add 0.50 µg/g of cobalt to air dry soil. The exact volume used was again adjusted to account for the soil moisture content.

The soils and cobalt solutions were mixed for 15 minutes in polypropylene buckets and then allowed to dry in air to around 15 per cent moisture content. Samples of untreated soil were also allowed to dry to this moisture content.

Three samples, weighing 1.2 kg from each of the treatments were placed in 13 cm diameter plastic pots. Thus for 12 soils there were 3 replicates for both control and cobalt sulphate treatments and 5 of the soils had, in addition, 3 cobalt EDTA treatment replicates.

Approximately 90 perennial ryegrass seeds (Lolium perenne L. var. S23) were sown in each pot. Fertiliser was applied to each pot in deionised water solution so that each pot had an addition equivalent to 40 ppm N, 8 ppm P, and 16 ppm K to the soil on an air-dry weight basis.

The soils were brought to a standard moisture tension of around 1.0×10^4 Pascals (≡ 7.5 cm Hg) using the moisture tension measurements described in section 7.1.4.

The soils were able to supply freely available water to the ryegrass, but were below field-capacity. This moisture tension was maintained throughout the experiment by the addition of deionised water to the pots.

The pots were covered with polythene sheeting until germination of the seeds and then the ryegrass allowed to grow for 60 days before harvesting using stainless steel scissors. The herbage samples from each pot were weighed, dried at 110°C, and then reweighed.

Analysis of the herbage samples for cobalt content was carried out as described in section 2.3; one sample per pot being analysed.

8.2 Results and Discussion

8.2.1 SOIL ANALYSES

The results of the soil analyses are presented in Table 4.1 of Chapter 4. The soils used in the present experiment were numbers: 2, 3, 5, 8, 11, 12, 13, 14, 15, 16, 19, 20.

8.2.2 PLANT COBALT ANALYSES

In Table 8.1 the dry matter mass and cobalt contents of the ryegrass sampled from all 3 treatments are presented.

Table 8.1. Ryegrass dry matter mass and cobalt content (Mean of 3 replicate samples).

	CONTROL		COBALT SULPHATE		COBALT EDTA	
SOIL	D.M.(g)	Co(μg/g)	D.M.(g)	Co(μg/g)	D.M.(g)	Co(μg/g)
2	4.8	0.07	5.2	0.07	-	-
3	3.8	0.13	4.4	0.22	4.2	0.43
5	4.3	0.09	4.9	0.17	4.1	0.20
8	3.1	0.16	3.2	0.48	-	-
11	3.4	0.08	3.6	0.08	-	-
12	4.6	0.05	4.9	0.05	-	-
13	3.4	0.06	5.1	0.12	-	-
14	3.7	0.05	4.4	0.11	-	-
15	4.0	0.09	4.8	0.13	-	-
16	4.6	0.29	4.6	0.87	4.3	0.76
19	4.8	0.05	4.7	0.30	4.8	0.15
20	3.0	0.11	3.2	0.51	3.2	0.46

There was no significant difference in the weight of herbage harvested between the different soil treatments. There was some variation in the weight of ryegrass harvested between soils, but this did not appear to have any significant effect on the cobalt concentration in the herbage. In the control treatments, the weight of herbage harvested was generally lower than that obtained in the pot experiment described in the previous chapter. The ryegrass in the previous experiment had reached a later stage of maturity as a result of better growing conditions.

The cobalt concentration in the 'control' herbage was generally about 60 per cent of that in the previous experiment, with a range of 30 to 100 per cent. The decreased herbage dry matter weight and cobalt concentration did not appear to be directly related, although the stage of

maturity would presumably affect the cobalt content. Increases in the concentration of plant cobalt with maturity have been noted by Beeson and McDonald (1951) in timothy grass and by Mitchell et al. (1957) in mixed herbage.

Although there were differences in plant cobalt content following cobalt application as the sulphate salt or EDTA complex, there is no evidence that one type of application was generally more effective than the other. This is in agreement with the observation of McLaren and Williams (1981) that Co-EDTA application was no more efficient than $CoSO_4$ in raising plant cobalt content.

It is evident, from Table 8.1, that in most cases the uptake of applied cobalt by the herbage was extremely small. For the cobalt sulphate additions the percentage of added cobalt assimilated by the herbage ranged from 0 to 0.44 per cent with a mean value of 0.10 per cent.

8.2.3 PLANT UPTAKE OF APPLIED COBALT IN RELATION TO SOIL PROPERTIES

Table 8.2 presents the correlation coefficients between the increase in plant cobalt resulting from $CoSO_4$ application and certain specific soil properties.

Table 8.2. Increase in plant cobalt concentration in relation to soil properties.

	pH_{H_2O}	% Fe	% Mn	C.E.C	% clay	% org C
Increase in plant Co concn.	xx -0.79	x -0.52	-0.47	0.06	x -0.58	0.33

xx $P < 0.01$
x $P < 0.05$

The increase in plant cobalt concentration was assumed to be the herbage cobalt concentration of the $CoSO_4$ treatments minus the cobalt concentration in the ryegrass of the control treatment. Table 8.2 indicates that the increase was dependent primarily on the pH of the soil and this relationship is demonstrated in Fig. 8.1. Appreciable amounts of applied cobalt were still taken up by plants above pH 6.0 in some soils. Nicholls and Honeysett (1964b) found no significant recovery of applied cobalt by clover or ryegrass when the soil pH exceeded 5.7. However, these authors applied less than a third of the quantity of cobalt used in the present experiment, and it was applied to the surface of the soils in pots. Adams et al. (1969) also noted that plant assimilation of applied cobalt decreased with increasing soil pH.

The importance of soil pH in this study is also shown by the high correlation ($r = 0.80$, $P < 0.01$) between the increase in plant cobalt concentration resulting from cobalt application and the plant cobalt concentration in untreated soils. The latter quantity was shown, in Chapter 7, to be highly dependent on soil pH.

It should be noted, however, that the plant uptake of added soil cobalt was, to some extent correlated with the clay, iron and manganese contents of the soils. The higher the concentrations of these fractions in the soil, the lower the uptake of added cobalt. Their importance was greater than that in the uptake of native cobalt, as seen from the results of the pot experiment described in Chapter 7.

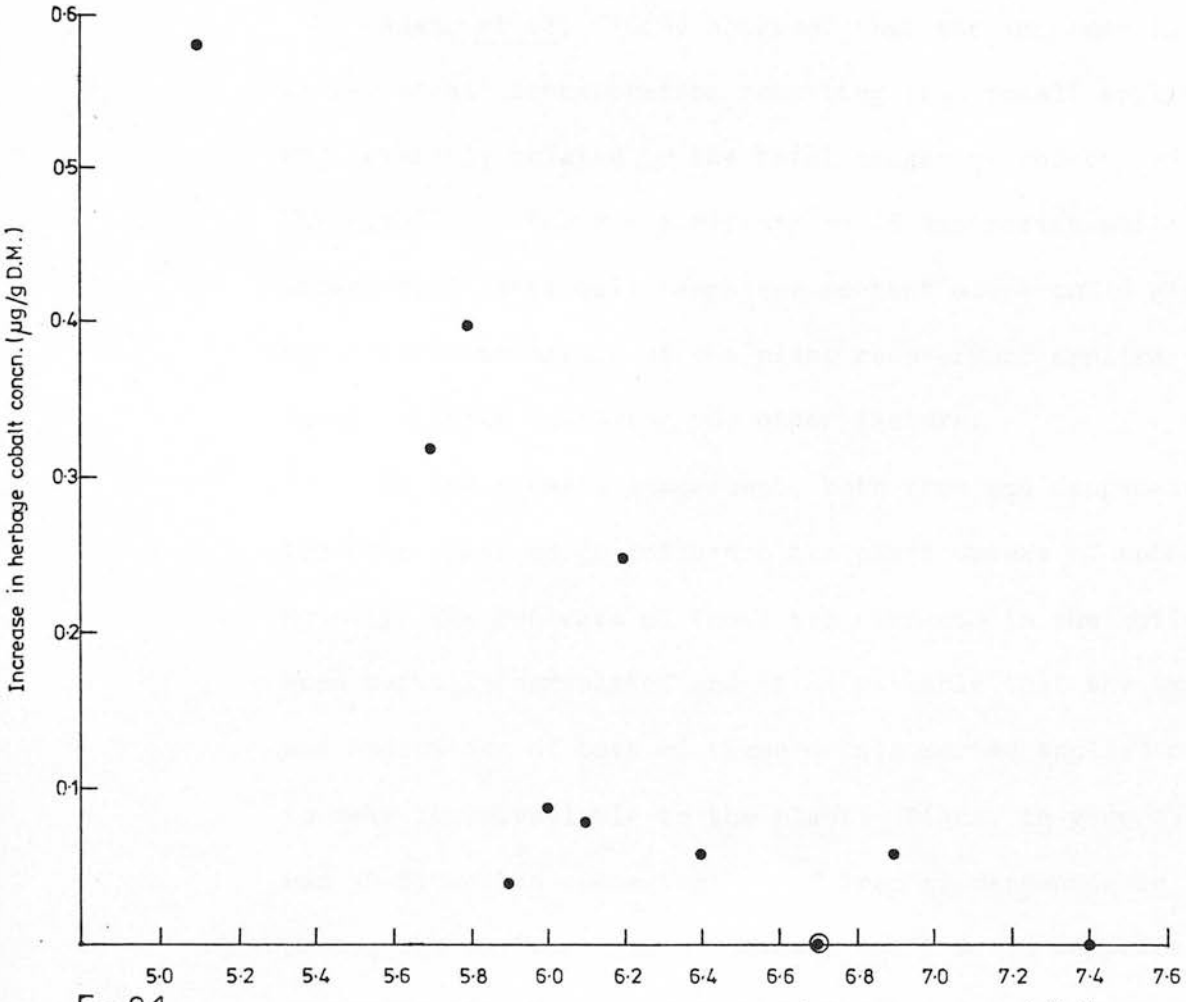


FIG 8.1

Relationship between the increase in cobalt content of ryegrass grown in pots and soil pH. Cobalt applied as $CoSO_4.7H_2O$ (0·5 µgCo/g soil).

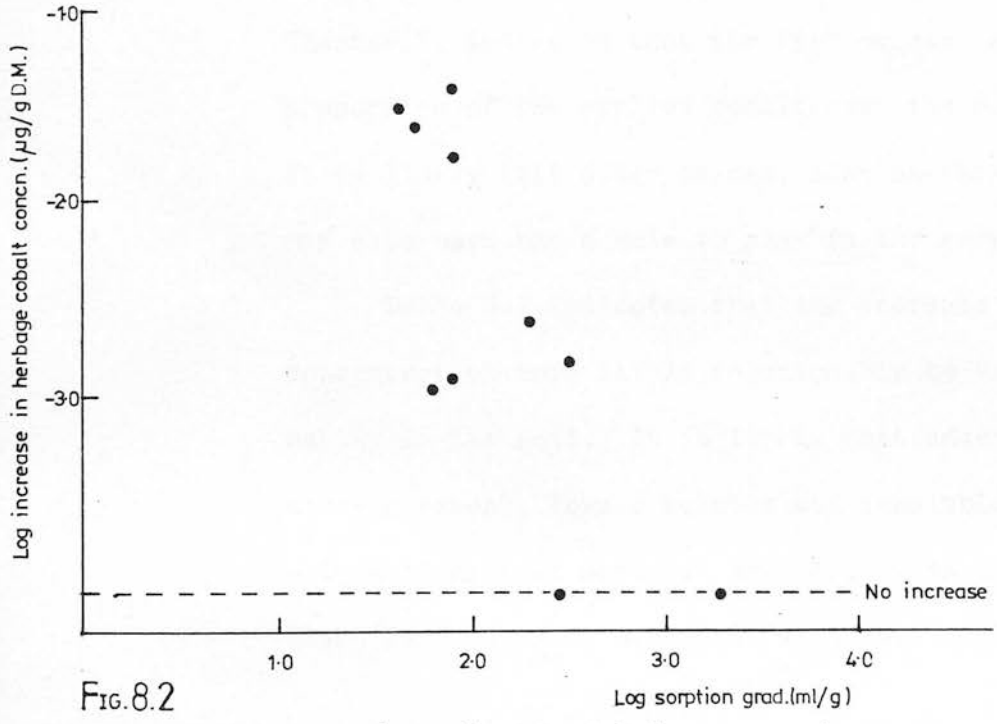


FIG. 8.2

Relationship between the log increase in cobalt content of ryegrass grown in pots and log soil cobalt sorption isotherm gradient.

Adams et al. (1969) observed that the increase in clover cobalt concentration resulting from cobalt application was inversely related to the total manganese content of the soil. The results of their experiments on 25 Australian soils showed that total soil manganese content alone could give a sufficient indication of the plant recovery of applied cobalt without involving any other factors.

In the present experiment, both iron and manganese contents appeared to influence the plant uptake of cobalt. However, the contents of these two elements in the soils were mutually correlated and it is probable that the oxides and hydroxides of both of these metals sorbed applied cobalt to make it unavailable to the plant. Since, in general, there was 50 times the concentration of iron as manganese in the soils, the surface area of oxide present would comprise predominantly of iron oxide. Initially, cobalt would be more likely to be sorbed by the soil iron oxides. The results of the soil moisture experiment, described in Chapter 5, indicated that the iron oxides sorbed a greater proportion of the applied cobalt than the manganese oxides. It is likely that other oxides, such as those of aluminium, may also have had a role to play in the sorption of cobalt.

Table 8.2 indicates that the increase in plant cobalt concentration bore little relationship to the amount of organic matter in the soil. It is likely that added cobalt, to a certain extent, formed soluble and insoluble complexes with soil organic matter. However, it is known that the stability constants of cobalt with soil organic matter fractions

are not so high as with other transition metals present in soil (Schnitzer and Skinner, 1967). Hodgson et al. (1965), in studying soluble low molecular weight organic matter complexes of cobalt, copper and zinc in soil, demonstrated that the proportion of complexed cobalt present in soil solution was low, as compared with copper and zinc.

8.2.4 PLANT UPTAKE OF APPLIED COBALT IN RELATION TO SORPTION OF COBALT BY SOILS

The cobalt sorption isotherms for 10 of the 12 soils used in this study are presented in Figures 6.6 and 6.7 of Chapter 6. The regression equations of the isotherms are supplied in the appendices. Table 8.5 presents the sorption isotherm gradient for 10 of the 12 soils.

Table 8.5. Log gradients of cobalt sorption isotherms.

SOIL	log grad. (ml/g)
2	3.30
3	1.82
5	1.94
8	1.63
11	2.46
12	-
13	2.51
14	-
15	2.32
16	1.87
19	1.93
20	1.69

The gradients of the sorption isotherms were shown, in section 6.3.4, to be related to soil pH and it is thus not unexpected that the log increase in plant cobalt from $CoSO_4$ application and log of the sorption isotherm gradients were correlated by a coefficient of -0.75 ($P < 0.02$). The relationship is shown in Fig. 8.2.

The cobalt applied to the soils in pots was equivalent to an addition of 0.5 μg Co per gram of soil. In the laboratory sorption experiments, the concentration of cobalt added to the soils was, at the most, 1.0 μgCo per gram of soil.

In both systems the type of bonding taking place between the added cobalt and soil is likely to have been the same and, as was seen in the laboratory sorption experiments, highly pH-dependent. Thus the dependence of ryegrass uptake of soil-applied cobalt on pH was a result of the extent of cobalt sorption by the soils. Most of the cobalt is specifically sorbed directly by the soil oxides and only a small proportion will enter back into solution. This proportion will increase as the soil pH decreases.

Adams et al. (1969) noted that the greatest increases in cobalt contents of clover were found on soils which had the greatest proportion of cobalt remaining in solution in their sorption isotherm studies. This is in agreement with the results of the present experiment, even although the quantities of cobalt added to the soil systems in the study by Adams et al. were much higher than in the present study.

8.3 Conclusions

The results showed that cobalt-EDTA soil application was, in general, no more effective than cobalt sulphate in increasing plant cobalt content. Cobalt-EDTA treatments might have been expected to be more effective because chelated cobalt should not enter into sorption reactions, with the soil's solid phase, in the same way that cobalt ions (Co^{2+}) do. Thus the chelated cobalt would remain

in solution where it could be absorbed by the plant root. The results suggest, however, that cobalt from the EDTA complex did in fact enter into the same reactions as the sulphate salt. This was probably a result of cobalt being displaced from the EDTA complex by other metal cations in solution such as iron and calcium.

Because of the greater cost of soil application of cobalt in chelated form, as opposed to the sulphate salt, it would seem to be more advisable to apply cobalt to pasture soils as cobalt sulphate.

The experiment on the plant uptake of native cobalt, described in Chapter 7, showed that on average 0.003 per cent of cobalt in the surface soil would be removed each year by pasture, if the results of the pot experiment were translated to field conditions. On the same basis, the results of this experiment show that if the increase in ryegrass uptake of cobalt was maintained for one year in the field, around 0.1 per cent of the applied cobalt would be removed from the soil.

It is therefore apparent that a very large proportion of the applied cobalt becomes non-available to plants. This is particularly true in soils with high pH.

The large effect of pH on the plant uptake of applied cobalt was a consequence of its effect on the solid phase sorption and desorption characteristics of cobalt. In Chapter 4 it was concluded that variation in soil pH affected the equilibrium between cobalt specifically sorbed on the soil oxides and in soil solution.

Although the iron and manganese oxide contents played a more important role in governing the concentration of applied cobalt which was plant available than with native cobalt, their importance

was still relatively small in comparison to soil pH. This was a consequence of the fact that only a small portion of the cobalt specific sorption sites on the soil oxides would be filled with the supplementary cobalt. Thus any increase or decrease in the concentrations of soil iron and manganese oxides would have had only a small influence on the amount of cobalt sorbed or remaining plant available.

The rectilinear form of the soils' cobalt sorption isotherms (Chapter 6, Figs. 6.6, 6.7) indicates that there was indeed a large excess of unfilled specific sorption sites for cobalt. Thus only a small proportion of the cobalt added to soils is likely to remain in a form in which it can be taken up readily by plants. This would be the case particularly at high pH.

CHAPTER 9.

THE UPTAKE BY HERBAGE OF COBALT APPLIED TO PASTURES IN THE BORDERS REGION OF SCOTLAND

In areas of the Borders region of Scotland where cobalt deficiency has been diagnosed in livestock, the general farming practice has been to top-dress pasture with $CoSO_4.7H_2O$ at the rate of 2 kg per hectare. This application is intended to maintain the herbage cobalt concentration above 0.08 μg Co per gram of herbage dry matter for 4 to 5 years. This is the minimum level regarded as being necessary for the maintenance of health in sheep.

In 1973 McLaren et al. (1979) conducted field experiments in the Borders region in which cobalt was applied by spraying cobalt sulphate onto pasture at 4 sites known to be deficient in cobalt. Each of the sites was on a different soil series. The plant uptake of the applied cobalt was measured and observed to vary greatly among the sites. The residual effect of the standard application of 2 kg/ha was noted to be short lived at all of the sites and after 2 years the pasture cobalt concentration had returned to below 0.08 ppm in all cases. On the basis of these results it was suggested that a greater amount of cobalt (6 kg/ha cobalt sulphate) should be applied to soils in order to maintain adequate pasture cobalt levels for ovine nutrition.

An experiment was designed to expand the scope of the above field trials to cover a number of sites on each soil series studied, with the object of determining whether the variations in responses to cobalt application were attributable to the soil series or to local site factors. The experiment also involved a comparison of the uptake by herbage of cobalt from an application of the metal sulphate with that of the metal-EDTA chelate.

Monitoring of the uptake of cobalt by pasture was carried out over a number of years and the cobalt content of the grass and clover species compared.

9.1 Experimental Method

The 15 trial sites were situated on the Lauder, Sourhope, Hobkirk and Ettrick soil series. All sites were under pasture, either for grazing or conservation.

Four of the sites were on the Ettrick soil series which is developed on grey and reddish-brown greywackes, flagstones and shales. It is a non-calcareous gley soil formed from till of fine texture and has poor drainage.

Five sites were on the Hobkirk series. This is formed from thin till of course texture which is derived from Upper Old Red Sandstone. It is a brown forest soil of low base status.

Two sites were on soils of the Lauder series. This series is formed on parent materials derived from Upper Old Red Sandstone conglomerates and sandstones. The soil is a brown forest soil of low base status developed from a shallow stony loam till over a solid conglomerate. It is freely drained.

Four sites were on the Sourhope soil series which is derived from andesitic lavas of Lower Old Red Sandstone age. These are mostly acid andesites. The soil is a brown forest soil of low base status which is based upon a reddish-brown rubble of loam texture.

Table 9.1. Analysis of soils from field trial sites

Site	Soil Series	$pH_{(H_2O)}$	% clay (<2μm)	% organic carbon	nitric/perchloric extractable Mn(μg/g)	Fe(%)	Co(μg/g)	acetic acid extble Co(μg/g)
Birkenside	Laud	6.2	17.7	1.52	396	2.27	11.28	0.24
Chapelhill	Ett	5.9	23.9	3.82	706	3.57	21.07	0.35
Clerklands	Ett	6.0	20.1	2.85	625	3.25	17.24	0.32
Colmsliehill	Ett	5.9	30.0	4.14	399	2.91	11.85	0.19
Corsbie	Hob	6.0	12.0	2.62	399	2.25	11.81	0.23
E. Nisbet	Hob	6.7	15.3	1.76	436	1.65	10.52	0.44
Fans	Hob	6.5	12.1	1.59	290	0.83	4.26	0.18
Gateshaw	Sour	5.0	19.7	5.64	607	2.29	16.32	0.20
Huntshaw	Laud	7.5	21.0	1.29	669	3.10	16.39	0.35
Lochtowers	Sour	5.8	15.0	4.83	541	2.29	13.43	0.45
O. Whitton	Sour	5.5	15.4	3.95	581	2.34	16.25	0.25
Scraesburgh	Hob	6.4	18.3	2.16	649	1.51	10.06	0.23
Swinnie	Hob	5.4	10.2	3.99	198	1.00	5.29	0.13
U. Chatto	Sour	5.3	16.6	3.83	566	1.99	13.03	0.21
Whitfield	Ett	5.6	25.5	4.49	998	3.59	21.72	0.21

Results of an analysis of the soils are presented in Table 9.1. The methods of analysis have been described in sections 2.1 and 2.2.1 of Chapter 2. The acetic acid soil extraction was carried out at an ambient temperature of 20°C.

Ordnance Survey grid reference co-ordinates for the sites are in the Appendices.

The applications of cobalt were made either in May or October 1978, when the pasture herbage was short. At each site, 3 treatments were applied to plots 20 m^2 in area:

1. $CoSO_4.7H_2O$ at 6 kg/ha which is equivalent to 1.26 kg Co/ha;
2. Co EDTA at 12.5 kg/ha which is equivalent to 1.25 kg Co/ha; and
3. Co EDTA at 1.0 kg/ha which is equivalent to 0.1 kg Co/ha.

The high concentration of Co EDTA was applied to supply the same amount of cobalt to the soil as the sulphate treatment. The low concentration of Co EDTA was that recommended by the manufacturers. All the applications were made from aqueous solution in a volume of 10 litres using a hand-pumped back spray.

The herbage was subsequently sampled using hand shears in June and October 1979, June 1980 and June 1981. The soil was sampled at random within the plots using a 20 cm screw auger, about 1 kg of moist soil being taken from each plot. This was carried out before application of treatments in October 1979, October 1980 and June 1981. Herbage and soil samples were taken from the field area surrounding the plots and used as 'control' samples. No herbage samples were taken where the pasture sward was so short that soil contamination of the sample was unavoidable.

In October 1980 soil cores were taken from the control areas and from the sulphate and high EDTA treatment plots. These cores were from the top 8 cms depth and the samples were split into four 2 cm sections and analysed for acetic acid-extractable cobalt.

The analysis for herbage cobalt and extractable soil cobalt were carried out as described previously in sections 2.3 and 2.4.2.

9.2 Results and Discussion

9.2.1 COBALT UPTAKE BY HERBAGE

The herbage cobalt concentrations for all sites at each sampling are presented in the appendices. It is suspected that in some samples there was contamination by soil or animal faecal matter. A small amount of soil contamination can cause a relatively large increase in the apparent plant cobalt concentration since the total soil cobalt concentration is generally about 10 to 50 times that in plant dry matter. The results from samples which have clearly been contaminated are not considered in the discussion.

Figures 9.1, 9.2, 9.3 demonstrate the response to cobalt top-dressing at each site. In most cases it can be observed that the herbage from the control areas was deficient in cobalt or was of borderline deficiency (~0.10 μg Co per g dry matter).

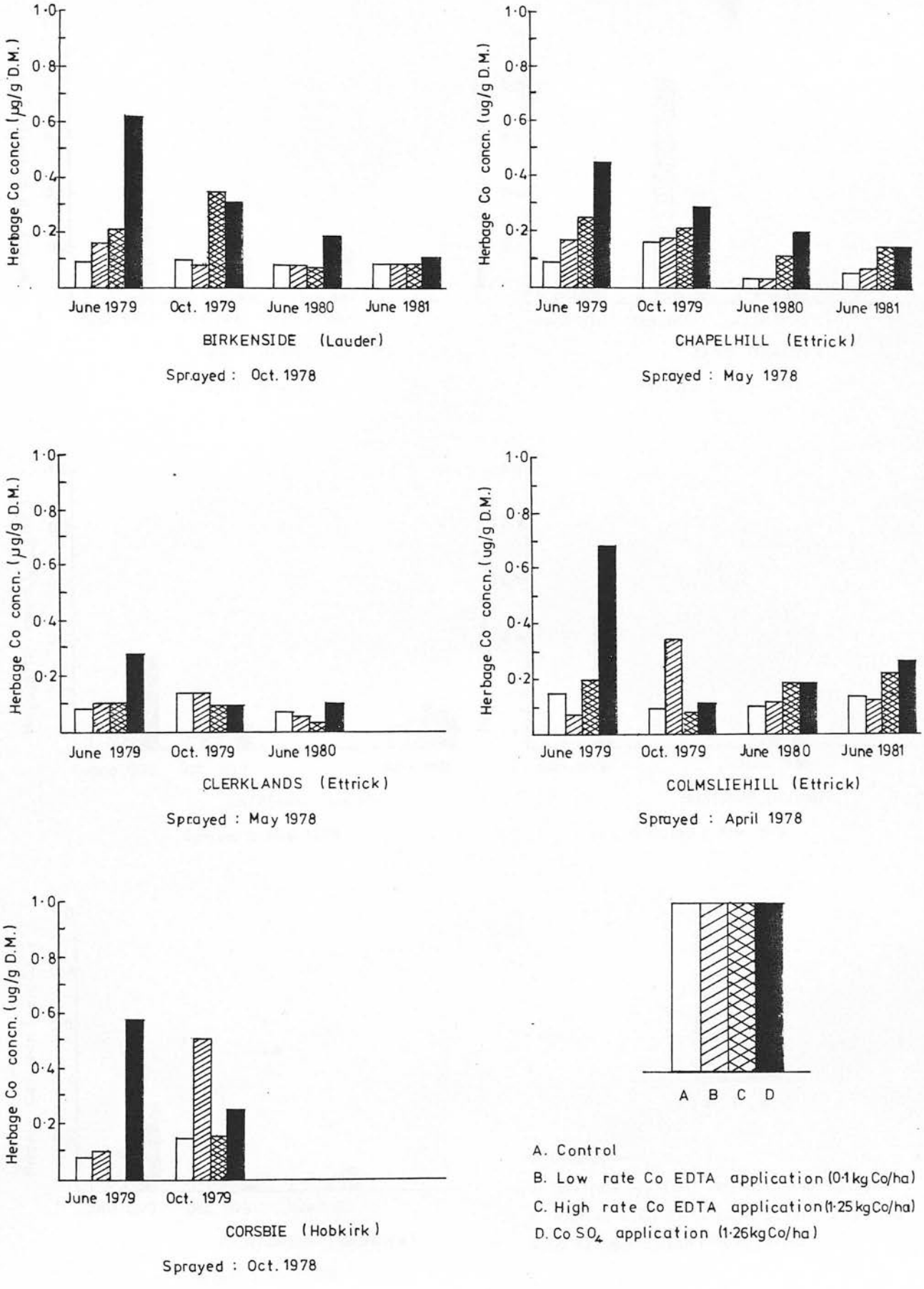


FIG. 9.1 Cobalt concentration in herbage at individual field trial sites in response to the top-dressing of pasture with cobalt.

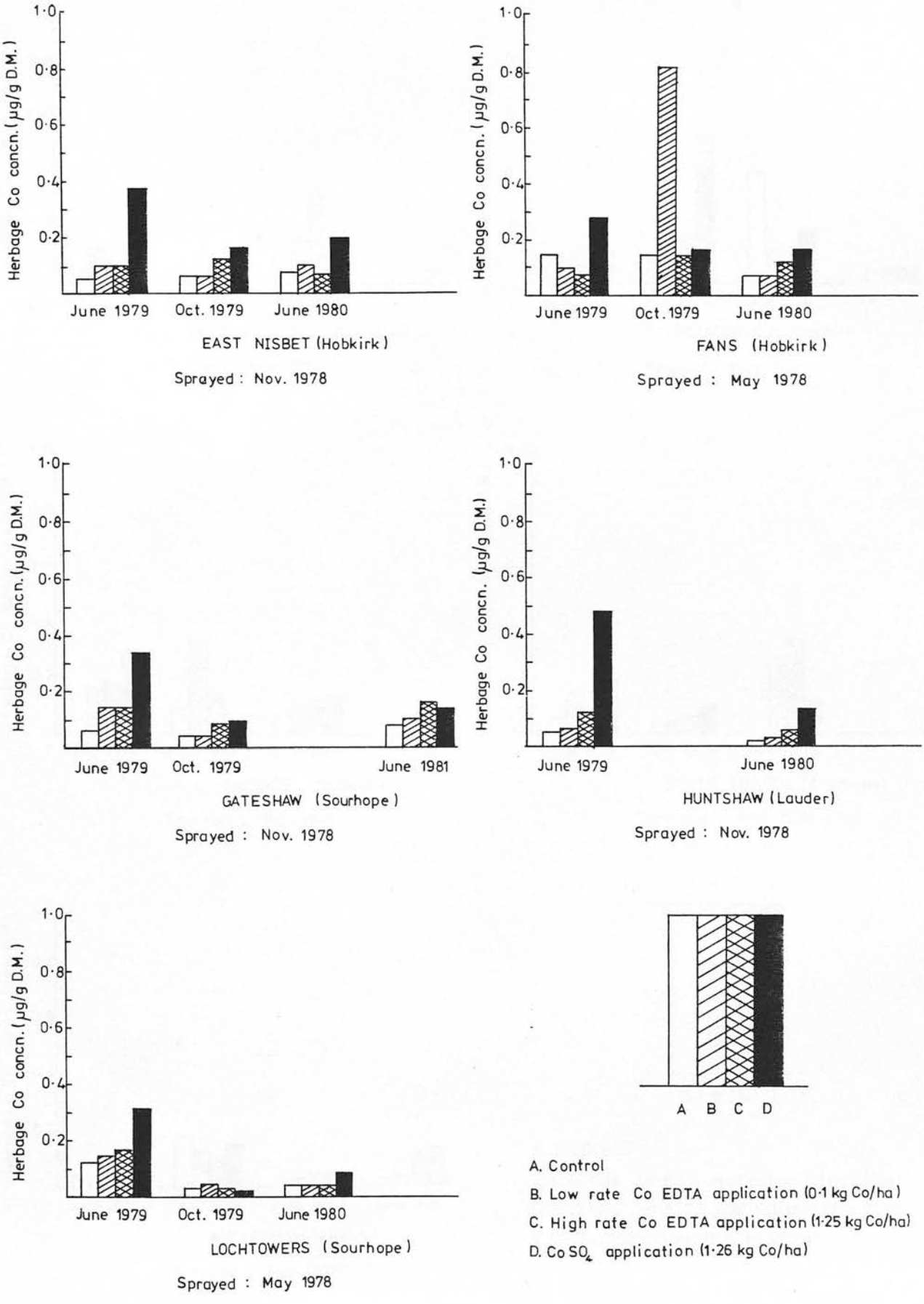


FIG. 9.2. Cobalt concentration in herbage at individual field trial sites in response to the top-dressing of pasture with cobalt.

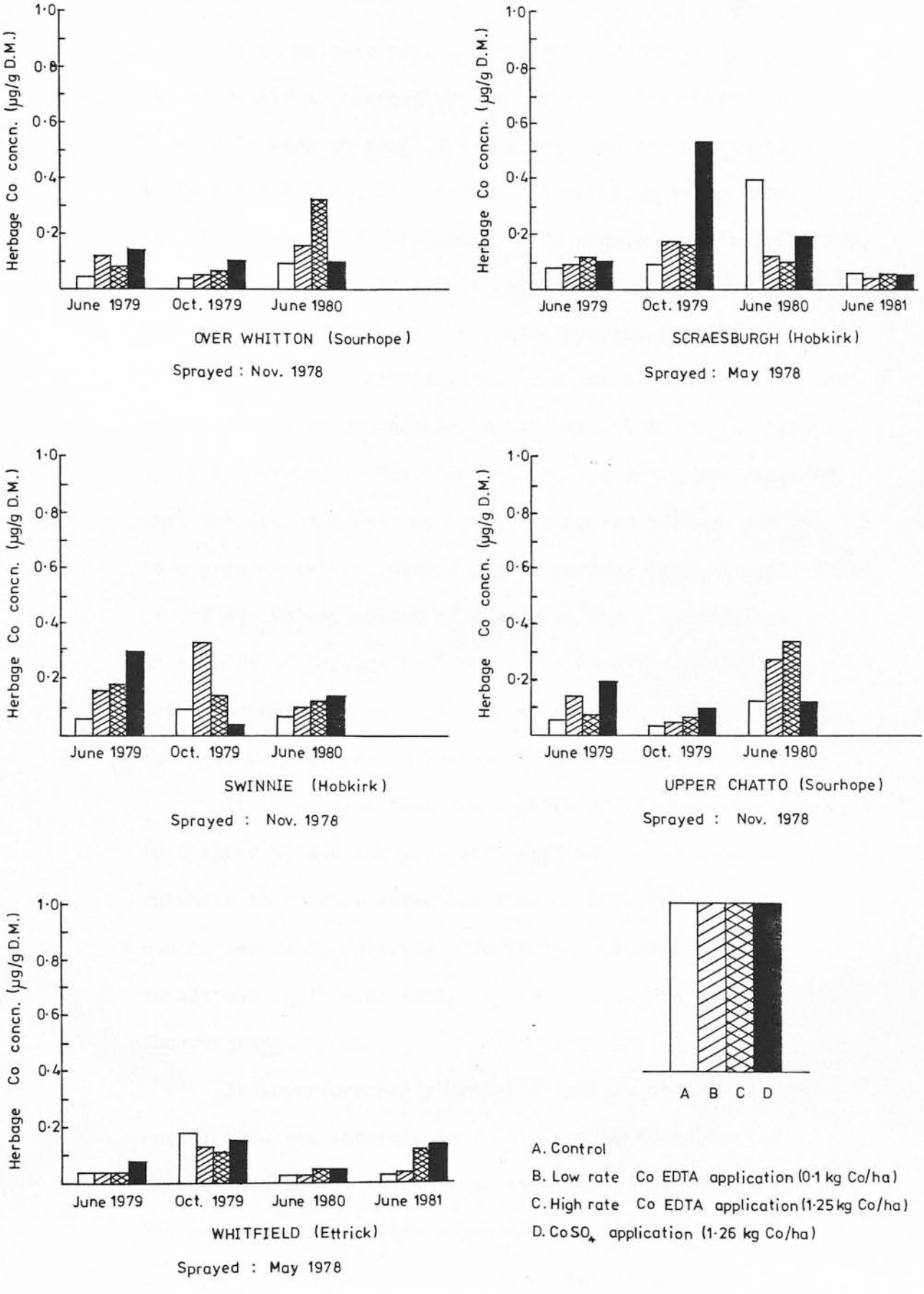


FIG. 9.3 Cobalt concentration in herbage at individual field trial sites in response to the top-dressing of pasture with cobalt.

It is evident that the sulphate treatment (6 kg/ha) was effective in increasing the herbage cobalt level to above 0.10 µg/g at most of the sites, and the increases in Co content were, in general, greater than those from the equivalent EDTA application. It should be noted, however, that in some cases the cobalt sulphate treated plots yielded cobalt-deficient herbage, for ovine nutrition, only 12 to 18 months after application. The low Co EDTA application caused little or no increase in the amount of cobalt taken up by the herbage. Reith and Mitchell (1964) also reported that the sulphate salt of cobalt increased herbage cobalt to a greater extent, over a 3 year period, than an application of the equivalent amount of cobalt as the EDTA complex. In samples of herbage analysed 3 months after pasture top-dressing, these authors found, however, that the cobalt contents were higher following the application of Co EDTA.

It is of note that the results of the pot experiment, in Chapter 8, did not show soil application of cobalt sulphate to be more effective than Co EDTA in raising cobalt levels in ryegrass. In the pot experiment the cobalt was applied directly to the soil before the growth of the ryegrass.

It therefore seems probable that in the field trials cobalt EDTA was absorbed by foliar uptake to a greater extent than cobalt sulphate at the time of top-dressing. The organo-metal complex would be more easily absorbed through the leaf cuticle than the metal salt. Thus, less

cobalt would enter into the soil, at the EDTA plots, to be available for subsequent plant uptake.

Initially the herbage cobalt concentration at the high Co EDTA treatment plots would have been high, but after being grazed, or cut for conservation, the cobalt levels would quickly decrease. The first herbage sampling was not soon enough after the time of application to detect the initial high concentrations of cobalt. It was mentioned above that Reith and Mitchell (1964) found a higher concentration of cobalt in pasture herbage top-dressed with cobalt-EDTA as compared to cobalt sulphate, when sampling was carried out 3 months after the cobalt application. In the present experiment, herbage sampling was carried out at least 8 months after cobalt application.

Table 9.2 presents the mean values for pasture herbage cobalt concentrations for each treatment at each sampling.

Table 9.2. Mean cobalt concentration in pasture herbage ($\mu g/g$ herbage D.M.)

sampling date	no. of sites	control	low EDTA	high EDTA	sulphate
June 1979	15	0.07	0.11	0.13	0.35
Oct. 1979	14	0.10	0.09	0.13	0.17
June 1980	13	0.07	0.08	0.09	0.14
June 1981	6	0.07	0.07	0.12	0.14

The values, in Table 9.2, again emphasise the greater ability of cobalt sulphate, as opposed to cobalt EDTA top-dressing, to increase herbage cobalt concentration. However, the sharp decrease in its effect, between June 1979 and October 1979, is also apparent from the table.

It is of note that the increase in plant cobalt content in the field trials was almost twice that in the pot experiment, described in Chapter 8, for the equivalent soil application of cobalt sulphate. This is despite the fact that, in the field trials, the herbage was sampled at least 8 months after cobalt application whereas in the pot experiment there was only a period of 2 months before cobalt application to the soil and plant sampling.

The differences in cobalt concentration could be partly attributed to the lower average pH of the field trial soils (6.0 as compared to 6.2 in the pot experiment soils) and to differences in moisture status between the field and pot experiment soils.

The increases in herbage cobalt content in June 1979 resulting from top-dressing with cobalt sulphate varied markedly from site to site. The increases in plant cobalt concentration ranged from 0.03 to 0.56 $\mu g/g$ D.M. and this variation cannot be attributed to soil series. Thus, localised variations in soil conditions or herbage were of greater importance, in influencing the uptake of applied cobalt, than differences in the basic soil type.

Table 9.3 presents a comparison of the cobalt concentration in clover species with that of grass species at the trial sites of East Nisbet and Huntshaw in June 1979.

Table 9.3. Cobalt concentration in grass, clover and mixed herbage at 2 trial sites. Sampled June 1979

SITE	Co concentration in herbage (μg/g D.M.)			
E. NISBET	CONTROL	LOW EDTA	HIGH EDTA	SULPHATE
mixed herbage	0.05	0.09	0.09	0.37
grass	0.04	0.06	0.07	0.32
clover	0.07	0.13	0.14	0.60
HUNTSHAW				
mixed herbage	0.05	0.06	0.12	0.48
grass	0.02	0.02	0.04	0.10
clover	0.10	0.16	0.29	0.47

Cobalt concentrations were greater in clovers than grasses on both control and cobalt treated plots. This effect was also reported by Reith and Mitchell (1964) and other authors have also reported an increased accumulation of soil cobalt by leguminous plant species as compared to grasses (Andrews, 1966; Beeson and McDonald, 1951).

In contrast to the results in Table 9.3 the results of the pot experiment in Chapter 7, showed that where perennial ryegrass was deficient in cobalt for ovine nutrition (< 0.08 μg/g D.M.) there was no significant increase in the level of cobalt in red clover growing on the same soil.

The contrasting results of the field and pot trials were possibly a result of the different plant growth conditions in the two experiments. In the glasshouse conditions of the pot trial, plant growth would be enhanced and so carbohydrate production in the plants would be relatively large compared to the assimilation of elements from the soil. Thus any

differences in the absorption of soil cobalt by the roots of red clover and ryegrass would not be reflected in the concentration of cobalt in the leaf dry matter.

Because of the comparatively slower rate of plant growth in the field situation there will be relatively smaller dilution, within the herbage dry matter, of the concentration of elements absorbed from the soil. Differences in the absorption of soil cobalt by the roots of clover and grass species will thus be apparent in the analysis of leaf material.

9.2.2 HERBAGE COBALT IN CONTROL AREAS IN RELATION TO SOIL PROPERTIES

With regard to the uptake by herbage of native soil cobalt, Figure 9.4 shows a plot of the mean herbage cobalt concentration in the control areas over the sampling period in relation to the soil pH of the sites. Above pH 6.0 the concentration of cobalt in the herbage decreased with increasing soil pH. It would be expected that, with increasing soil pH soil cobalt would be more strongly sorbed to the solid phase of the soil. However, this relationship did not extend to soil pH values below 6.0, where the plant cobalt concentration tended to decrease with decreasing soil pH. This is in contrast to the results of the pot experiment described in Chapter 7, which showed ryegrass cobalt contents to be negatively correlated with soil pH over the pH range 5.0 to 7.4.

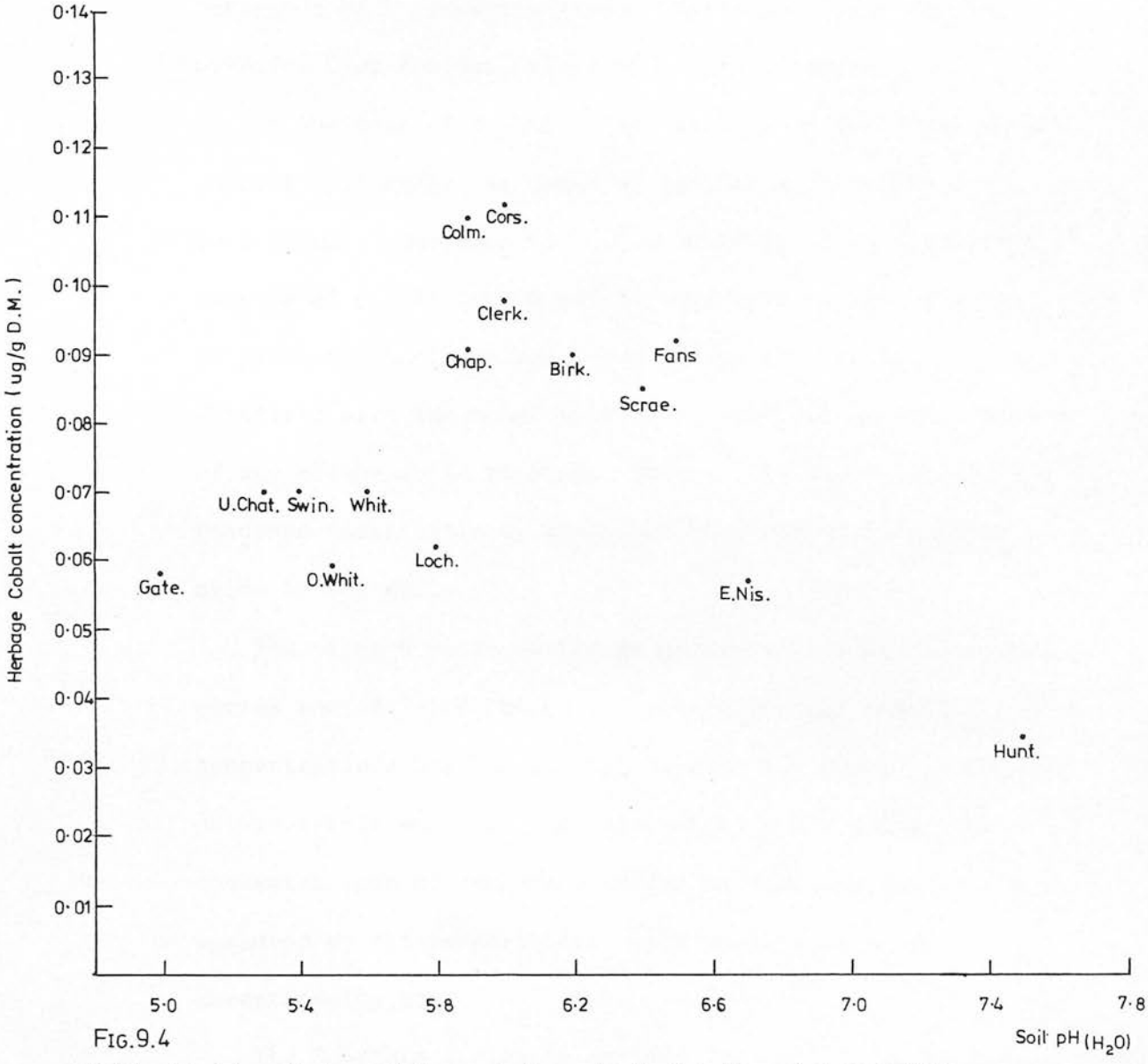


FIG. 9.4

Relationship between herbage cobalt concentration and soil pH in the control areas of the field trial sites.

Six of the field trial sites had unexpectedly low herbage cobalt concentrations:- Gateshaw, Upper Chatto, Swinnie, Over Whitton, Whitfield and Lochtowers.

In the case of Swinnie there was a very low total cobalt content (5.3 μg/g), as measured by nitric/perchloric acid soil digest. Consequently there would not be a sufficient reserve of cobalt in the soil to maintain an adequate pool of plant-available cobalt, even at low pH. At the Whitfield site the total soil cobalt content was the highest of any of the soils studied. However, it was probably rendered unavailable by the large quantity of manganese oxide in the soil.

The other 4 soils in the group are of the Sourhope soil series and, despite having relatively average cobalt concentrations and low soil pH levels, the plant uptake of native cobalt was low. In relation to other sites the concentrations of manganese oxides and iron oxides, as measured by nitric/perchloric acid digest, were not exceptionally high.

The Sourhope series is derived from andesitic lavas and these contain a large quantity of pyroxenes, along with hornblende, biotite and olivine. In the formation of igneous rocks cobalt associates itself with the ferromagnesian minerals such as the pyroxenes and it substitutes within the mineral for Mg, Fe or Mn ions. On weathering of the rock to form soils much of the cobalt will be present in these

primary minerals and this fraction will remain relatively unreactive in the soil. Much of this cobalt will be extracted by nitric/perchloric acid digest and some by acetic acid but, in contrast with cobalt present in the amorphous oxide fraction, the cobalt will not be affected to any great degree by change in soil pH or redox reaction of the soil. Because of the greater stability of these primary minerals a smaller proportion of the associated cobalt will become plant-available in soils of this series, even at low pH.

Overall, there was no significant correlation between the concentration of herbage cobalt and the soil manganese and iron oxide contents in the 15 soils. This result was also observed in the pot experiment described in Chapter 7.

9.2.3 INCREASE IN HERBAGE COBALT FROM COBALT SULPHATE APPLICATION IN RELATION TO SOIL PROPERTIES

The increase in the mixed herbage cobalt concentration resulting from cobalt sulphate application was not significantly correlated with soil pH. This is in contrast to the results of the pot experiment in Chapter 8, which showed that the uptake of supplementary soil cobalt by ryegrass was negatively correlated with soil pH. It was also concluded from the results of the isotopic exchange studies, in Chapter 4, that the amount of cobalt entering into solution from the solid phase was indirectly related to soil pH.

In the pot experiment, described in Chapter 8, it was also shown that the increase in plant cobalt concentration resulting from cobalt sulphate application to soil, was negatively correlated with the concentrations of clay and

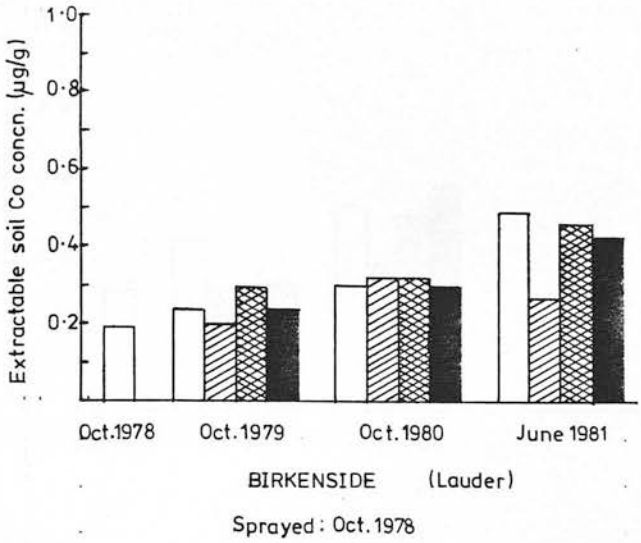
the oxides of iron and manganese. This was not the case in the present experiment.

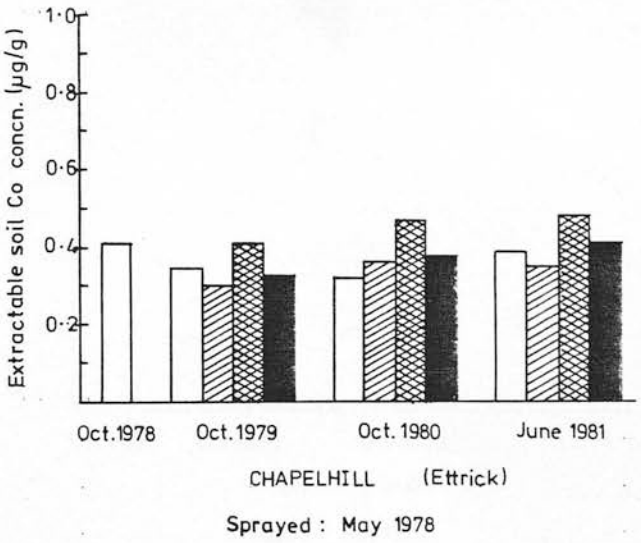
It is evident that in the field situation the plant-availability of applied cobalt is largely influenced by other factors, such as soil moisture status. It is also probable that the different methods of cobalt application used in the pot and field trials influenced the form in which applied cobalt was held by the soil and subsequently became plant-available.

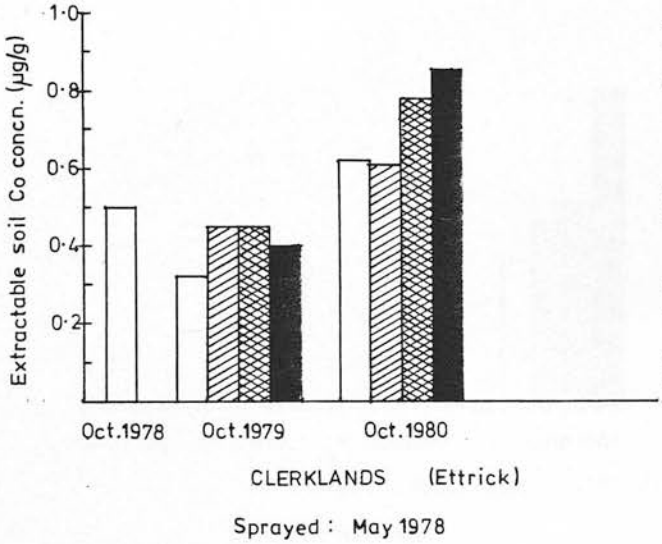
9.2.4 ACETIC ACID-EXTRACTABLE SOIL COBALT

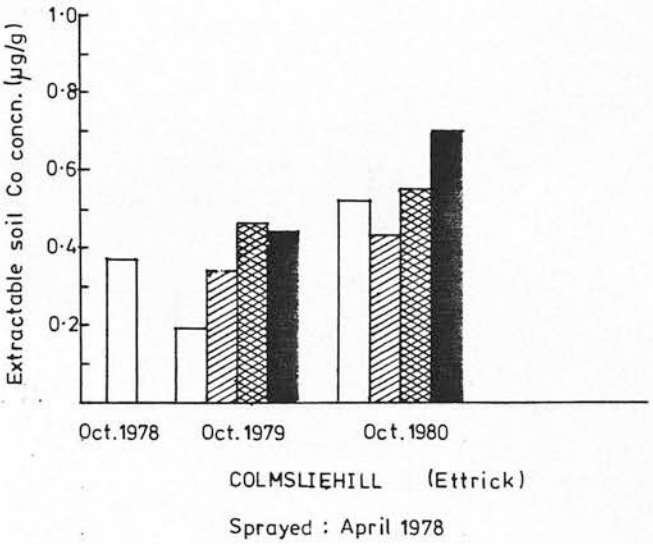
Figures 9.5, 9.6, 9.7 show the extractable soil cobalt levels of the plots at each site over the period of the experiment. The initial sampling was carried out in the 60 m^2 plot area and the 'control' area before spraying the cobalt solutions onto the pasture.

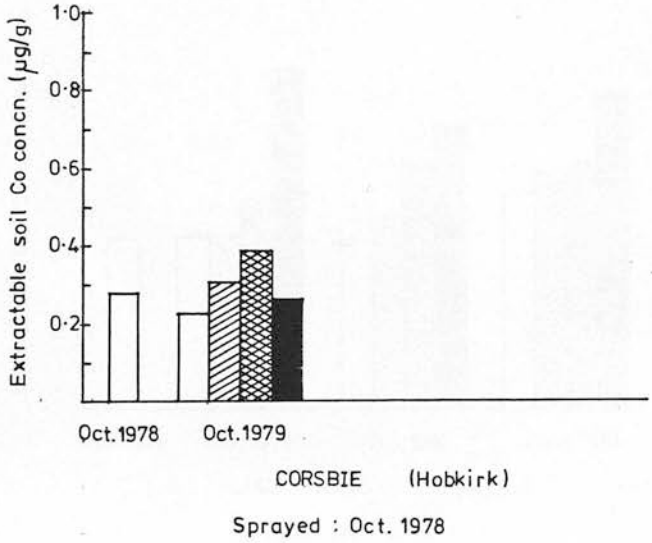
Although in some cases the acetic acid-extractable soil cobalt levels in the control areas remained constant during the experimental period, in many cases there was considerable variation. This may have been caused by variation in the extractable native cobalt levels, perhaps as a result of varying soil moisture conditions between sampling times. Mitchell et al. (1957) noted that more cobalt was extracted, by 0.5 M acetic acid, from a poorly drained soil than a well drained soil in the same vicinity. The results of the soil moisture experiment in Chapter 5 showed the levels of cobalt extractable by acetic acid to increase dramatically when waterlogged conditions were present.

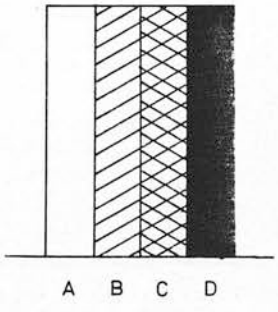












A. Control

B. Low rate Co EDTA application (0·1 kg Co/ha)

C. High rate Co EDTA application (1·25kg Co/ha)

D. $CoSO_4$ application (1·26 kg Co/ha)

FIG. 9.5 Concentration of soil cobalt extractable by 0·5 M acetic acid at individual field trial sites after the top-dressing of pasture with cobalt.

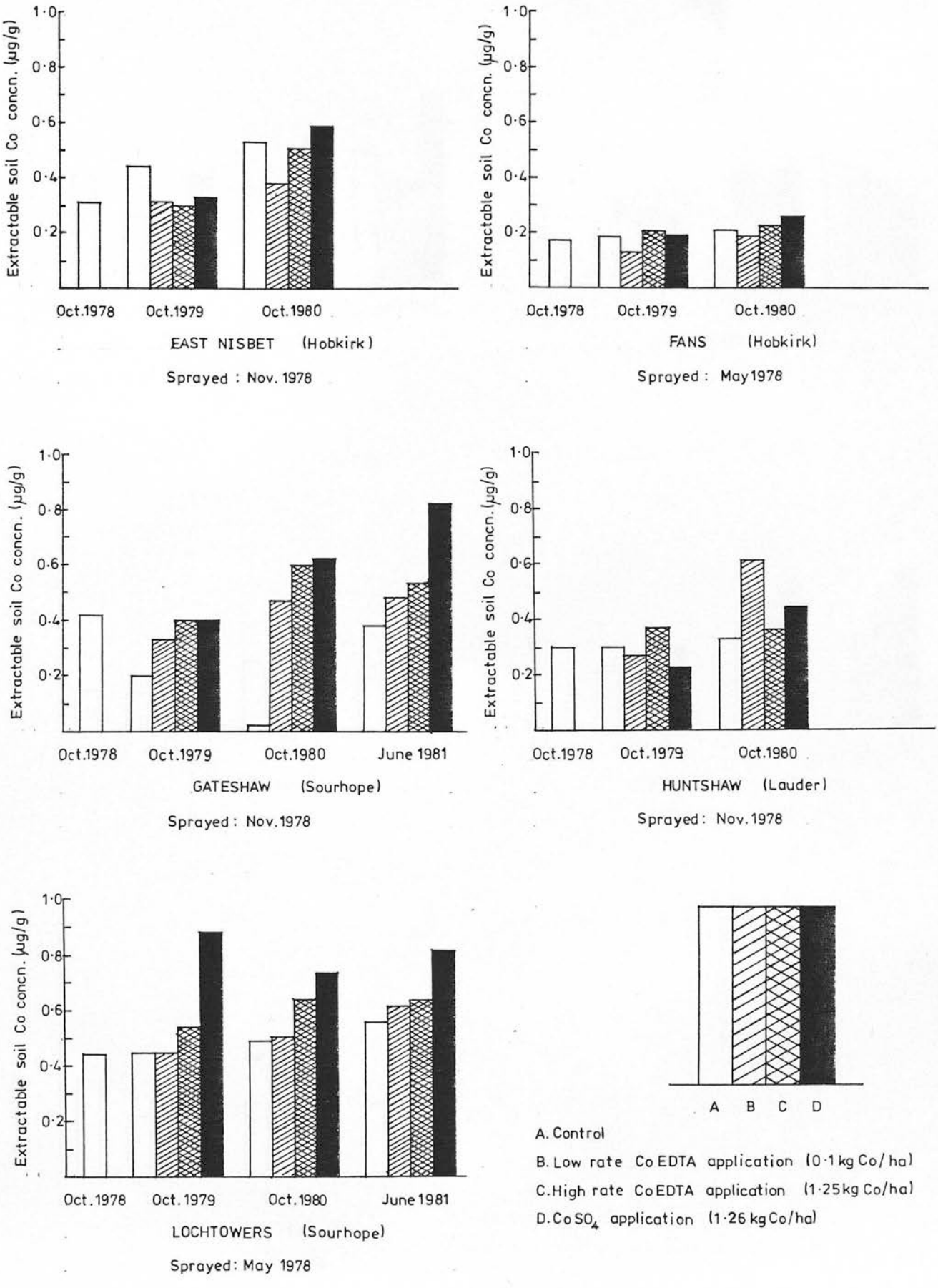


FIG. 9.6 Concentration of soil cobalt extractable by 0·5M acetic acid at individual field trial sites after the top-dressing of pasture with cobalt.

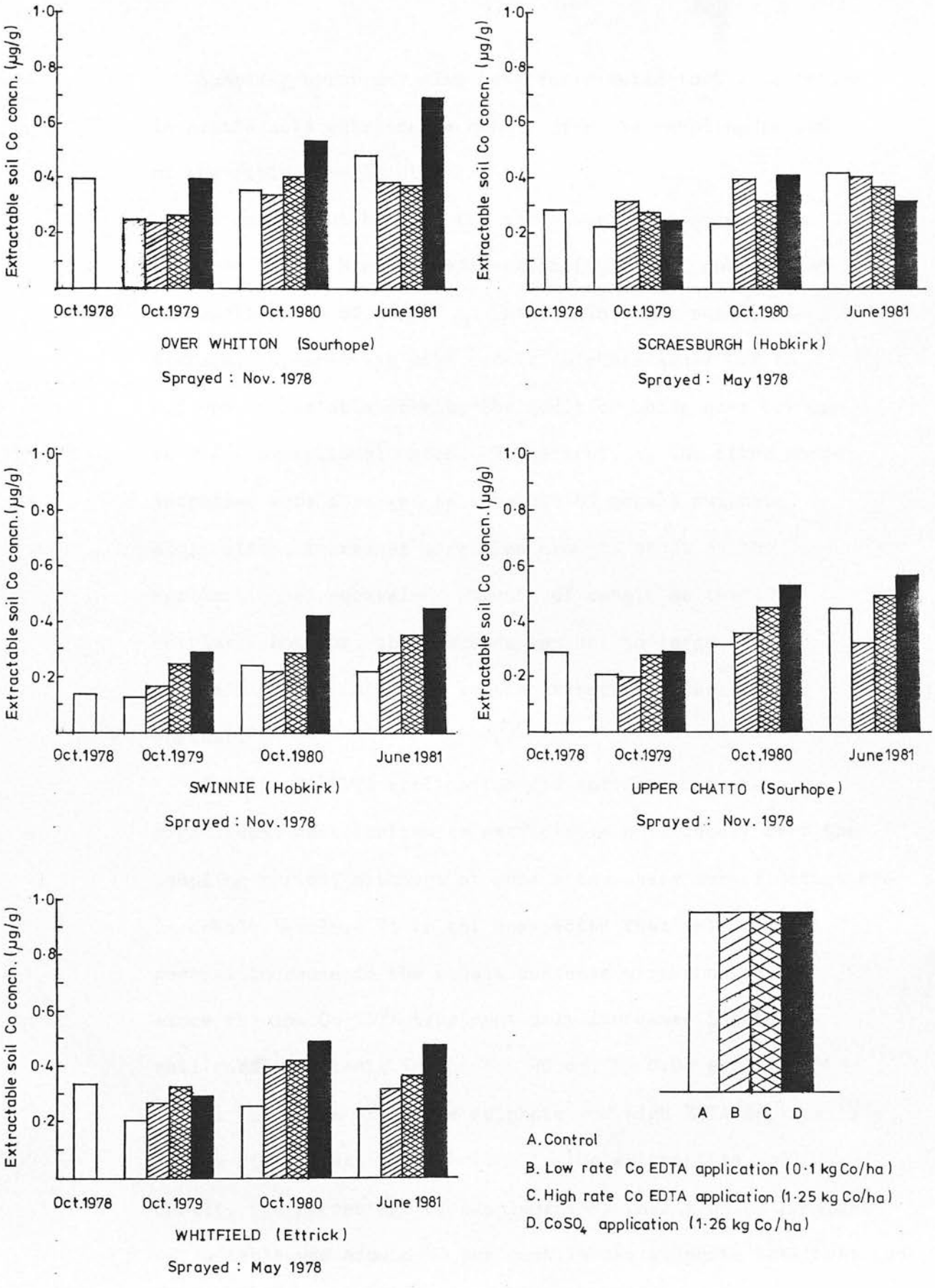


FIG.9.7 Concentration of soil cobalt extractable by 0·5M acetic acid at individual field trial sites after the top-dressing of pasture with cobalt.

Sampling error may also have contributed to the variation in acetic acid extractable cobalt over the sampling period of the field experiment.

At only about half of the sites was there an obvious increase in 0.5 M acetic acid-extractable soil cobalt from the application of cobalt sulphate. In these soils, on average, top-dressing with cobalt sulphate added 0.2 to 0.3 ppm extractable cobalt, the addition being over 0.4 ppm in a few exceptional cases. In general, at the sites where increases were observed as a result of cobalt sulphate application, increases were also brought about by the application of equivalent amounts of cobalt as the EDTA complex. However, the increase was not so large, being around a 0.1 ppm addition to the extractable soil cobalt content.

The low Co EDTA application did not appear to make a significant contribution to extractable soil cobalt over the sampling period, although at some sites there were fluctuations in cobalt levels. It is not unexpected that only a small general increase in the cobalt contents were observed, since the low Co EDTA treatment only increased the total soil cobalt content, in the top 20 cm, by 0.04 ppm.

At the sites where the sulphate and high EDTA applications made a significant contribution to the extractable soil cobalt, the percentage of supplementary cobalt which remained extractable was around 40 per cent in the sulphate treatment and 20 per cent in the EDTA treatment. In almost all of these

cases its extractability was maintained for at least $2\frac{1}{2}$ years after top-dressing.

The results of the soil moisture laboratory experiment in Chapter 5 showed that, where cobalt was added to soil, its extractability by acetic acid decreased over a period of 8 months even with intermittent waterlogging of the soil. In 2 of the 3 soils studied the extractability of added cobalt decreased to 10 per cent and 30 per cent.

An important factor is likely to have been the different methods of cobalt application in the laboratory and field experiments. In the soil moisture experiment cobalt was applied to communited soil and was therefore allowed to interact with all of the soil fractions. In the field experiment the cobalt was applied to the surface of the soil where the organic matter levels were higher than in the bulk of the soil. Cobalt would be sorbed to a large extent by the organic matter at the surface. The results of the cobalt sorption experiments in Chapter 6 showed that humic and fulvic acids had a high capacity for cobalt sorption. However, cobalt was more easily desorbed back into solution and remained more isotopically exchangeable in these materials than in the inorganic soil separates. Therefore, cobalt sorbed onto the organic matter fraction at the surface of the pasture soils is likely to be easily desorbed into acetic acid solution whereas cobalt sorbed at both the organic and inorganic fractions, as in the soil moisture experiment, may become less extractable by acetic acid. The cobalt sorption experiments in Chapter 6 showed that cobalt sorbed

to soil oxides and montmorillonite became bound with higher energy over time. In addition, there is evidence to indicate that cobalt entering the fermentation layer at the soil surface would remain more extractable than cobalt at lower depth, even although cobalt, in both cases, was bound to inorganic components. Ng and Bloomfield (1962) reported that the extractability of soil cobalt by 2.5% acetic acid was increased in the presence of decomposing plant material. The concentrations of solution manganese and iron in soil were also found to increase in the presence of decomposing grass.

It has been concluded, in Chapters 5 and 6 that cobalt applied to soil becomes predominantly associated with iron and manganese oxides. The positive relationship between extractable native soil cobalt content and manganese and iron is shown in Fig. 9.8 for the field experiment soils.

This positive relationship is not unexpected as the total native cobalt content of the soils (as measured by nitric/perchloric acid digest) was correlated with the iron and manganese oxide contents. The correlation coefficients were 0.91 ($P < 0.001$) and 0.87 ($P < 0.001$) respectively.

The stability of these oxides in the soil fermentation layer is likely to be lower than at greater depth and so they would be more soluble in acetic acid. The extractability of associated cobalt would also remain high. This phenomenon, along with the high extractability of cobalt associated with organic matter, would ensure that cobalt applied to the surface of permanent pasture remains extractable by acetic acid.

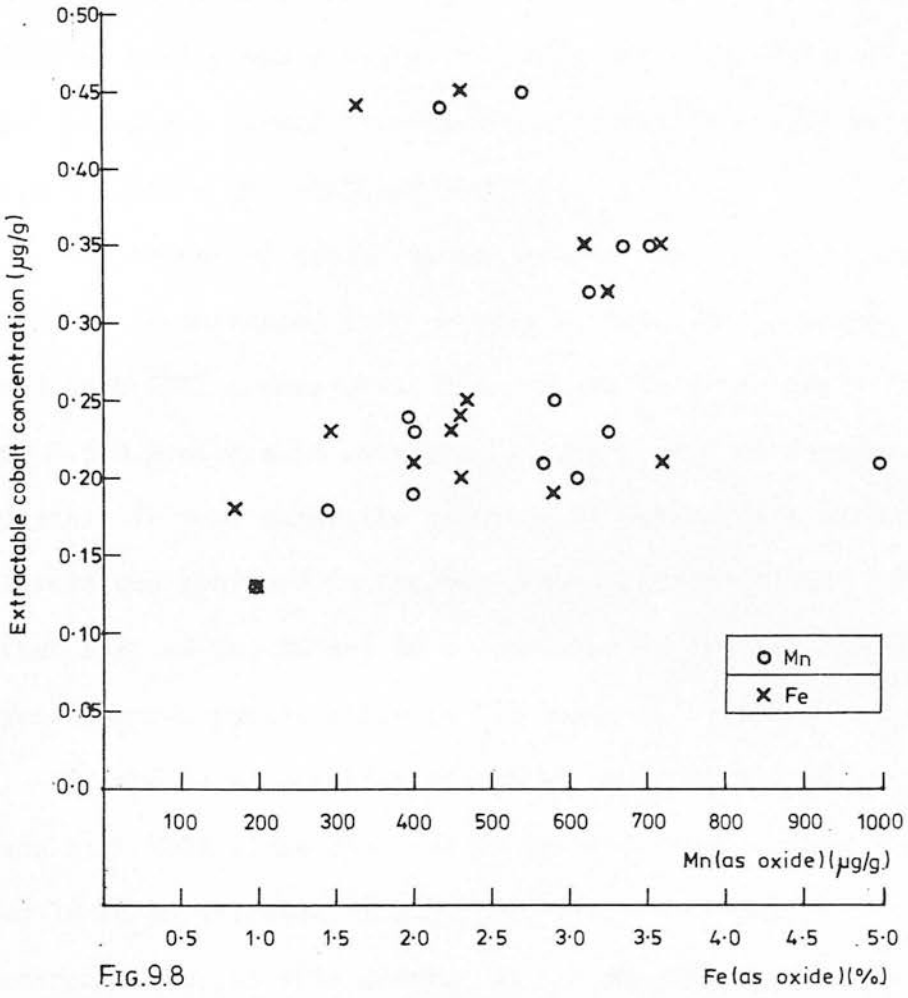


FIG.9.8

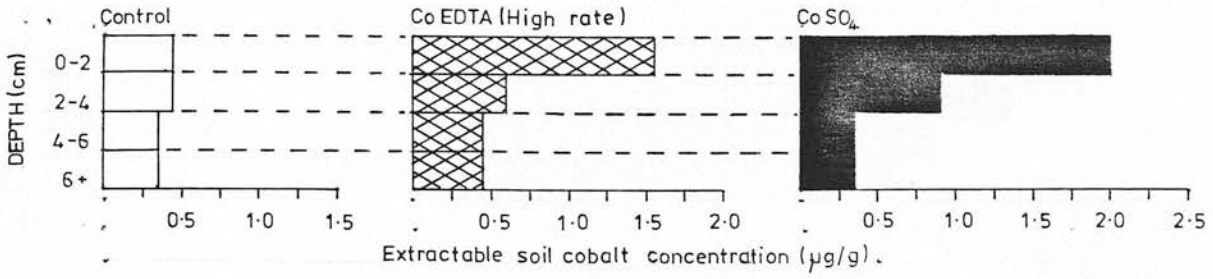
Relatationship between the concentration of soil cobalt extractable by 0·5M acetic acid and the soil manganese and iron oxide contents in the control areas of the field trial sites.

It is of interest that the 4 sites on the Sourhope soil series showed significant increases in extractable soil cobalt as a result of cobalt sulphate application, as did 3 of the 4 sites on the Ettrick series. Of the 5 sites on the Hobkirk series and 2 on Lauder, only one site (Swinnie) exhibited any marked increase in extractable cobalt contents.

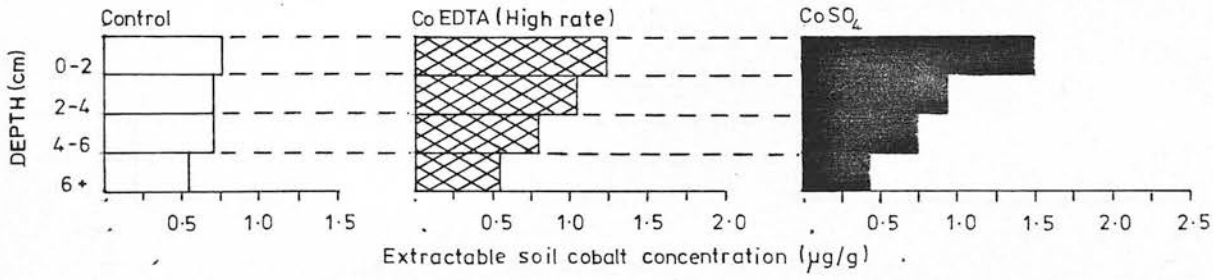
9.2.5 DEPTH OF COBALT MOVEMENT

The extent of cobalt movement into the soil by October 1980 is demonstrated in Figures 9.9, 9.10, 9.11 for the sulphate and high EDTA treatments. The results show the concentration of 0.5 M acetic acid extractable cobalt at 2 cm intervals of depth. In most cases the increase in extractable cobalt levels was confined to the top 4 cms. Forbes (1976) observed that applied Co, Cu and Zn accumulated in the top 7.5 cm of yellow-brown pumice soils in New Zealand.

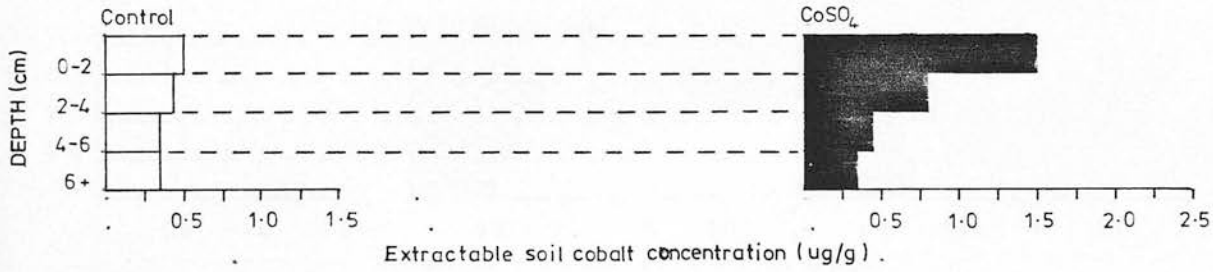
If the total quantity of cobalt added to the sulphate and high EDTA plots remained in the top 4 cm of soil there would be an increase of 2.5 ppm in the total cobalt concentration to this depth. At the Huntshaw site, in which the results were typical of most sites, the extractable cobalt in the top 4 cm increased by 1 ppm with $CoSO_4$ topdressing. A proportion of the added cobalt would become non-extractable because of its incorporation into the soil minerals and so it would appear that a considerably large part of the cobalt sprayed onto the pasture, as the sulphate salt, entered into the soil. Exceptions to this were at the Fans and Gateshaw sites. At the Gateshaw site there appears



CHAPELHILL (Ettrick)

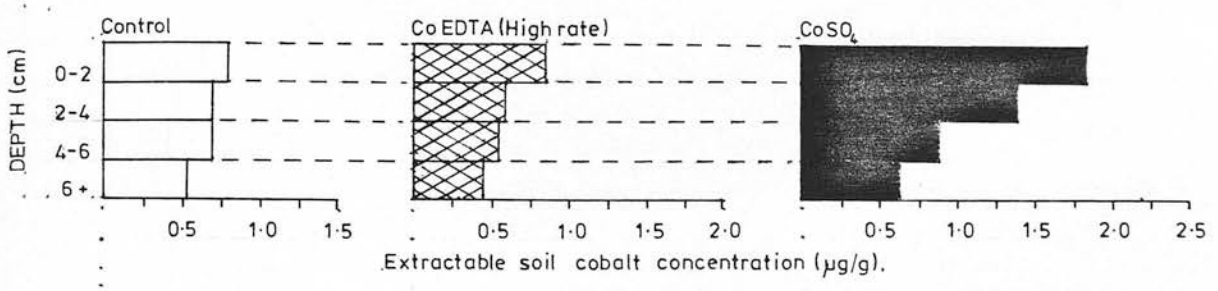


CLERKLANDS (Ettrick)

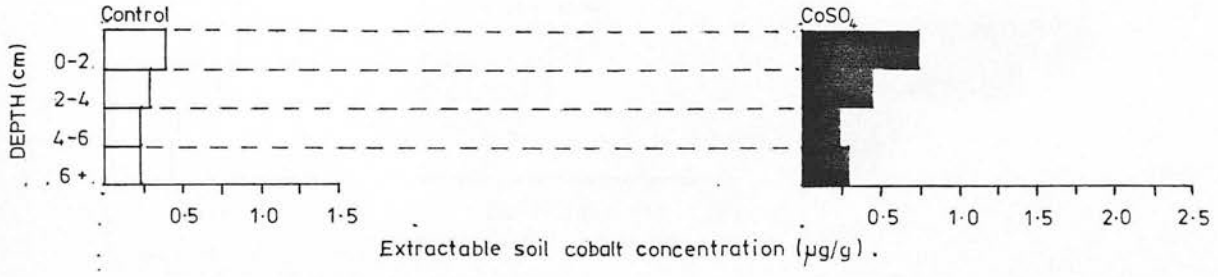


COLMSLIEHILL (Ettrick). (Sampled : May 1980)

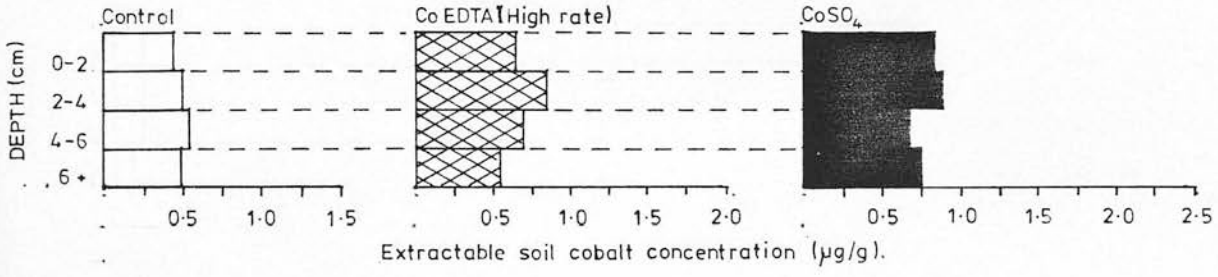
FIG. 9.9 Variation with depth of the 0·5M acetic acid-extractable soil cobalt concentration. (Oct. 1980)



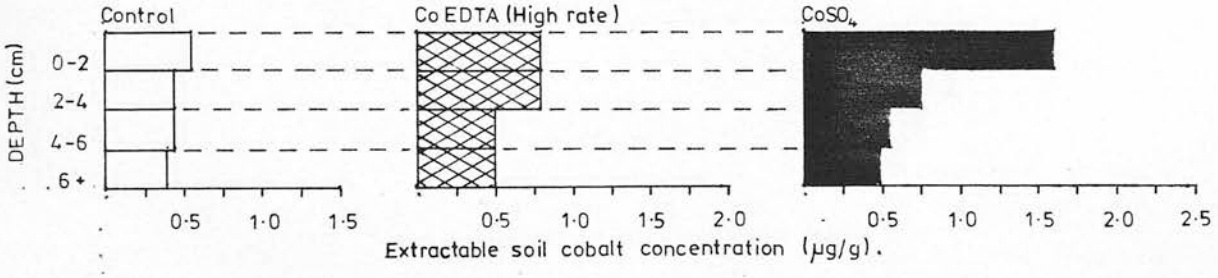
EAST NISBET (Hobkirk)



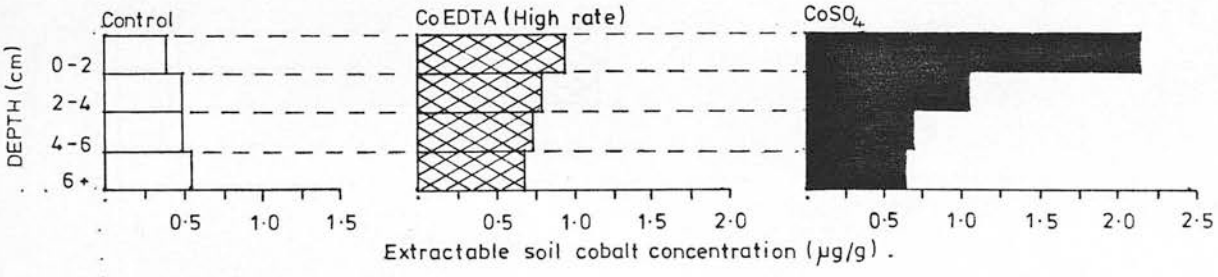
FANS (Hobkirk)



GATESHAW (Sourhope).

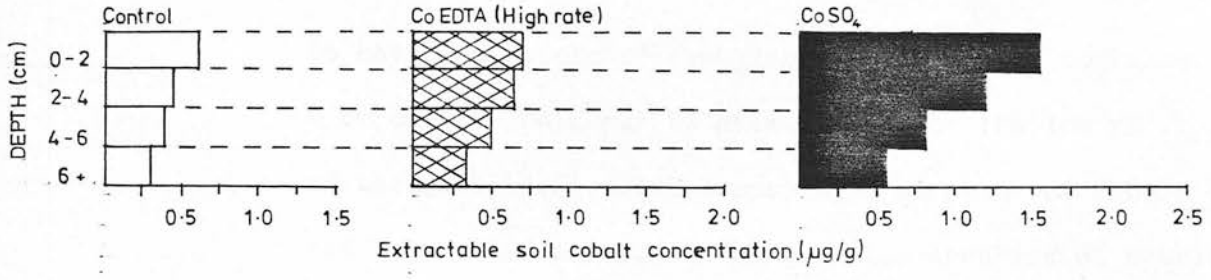


HUNTSHAW (Lauder)

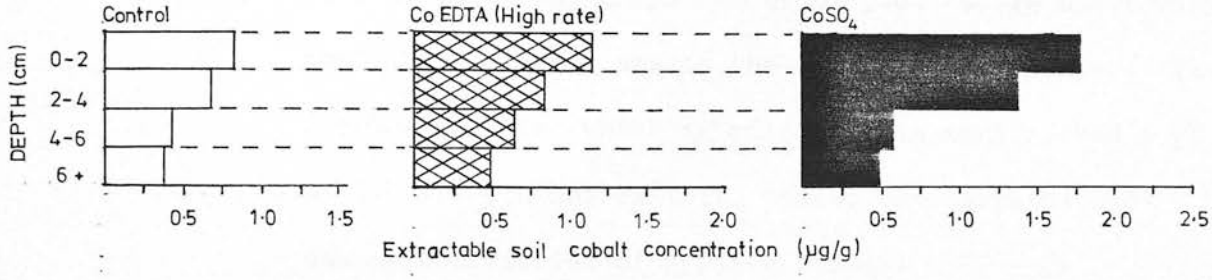


LOCHTOWERS (Sourhope)

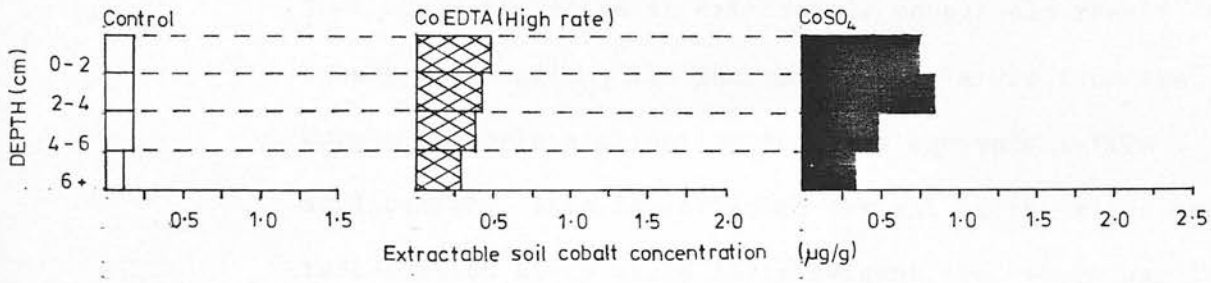
FIG. 9.10 Variation with depth of the 0·5M acetic acid-extractable soil cobalt concentration.(Oct.1980)



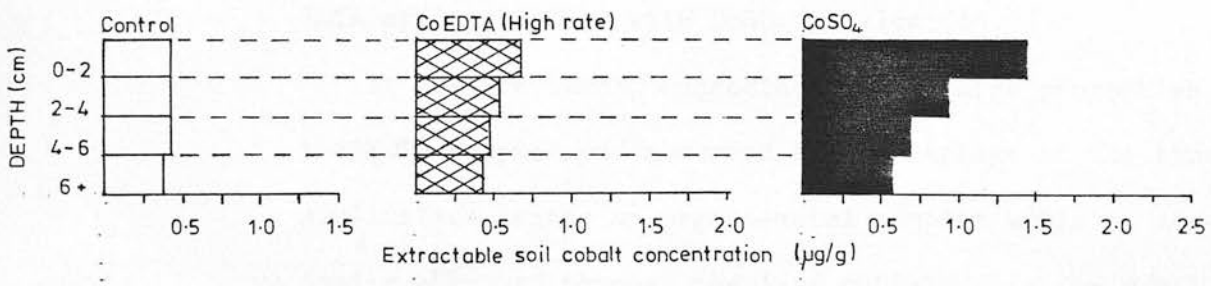
OVER WHITTON (Sourhope)



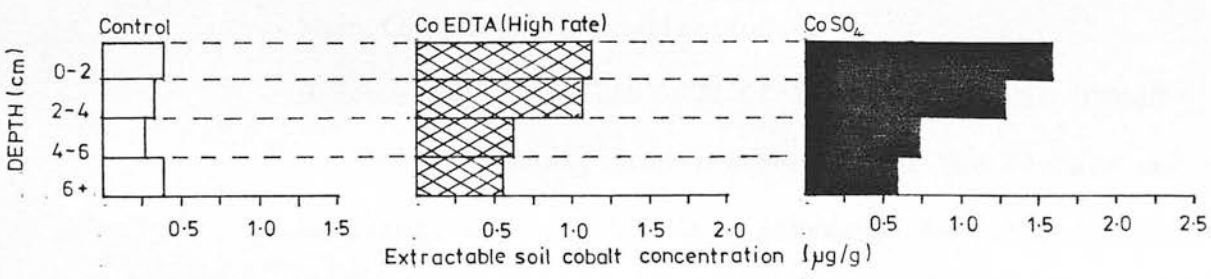
SCRAESBURGH (Hobkirk)



SWINNIE (Hobkirk)



UPPER CHATTO (Sourhope)



WHITFIELD (Ettrick)

FIG.9.11 Variation with depth of the 0·5M acetic acid-extractable soil cobalt concentration. (Oct.1980)

to have been a significant leaching of cobalt to below 4 cm depth. This may be attributable to the low pH of the soil (5.0) which discouraged sorption of cobalt by the soil solid phase. There was also leaching of cobalt to below 6 cm in the Over Whitton and Upper Chatto sites, both of which had pH values below 5.6. It is noteworthy that these 3 sites are on the Sourhope soil series. The Lochtowers site, which is also on this series, had a pH of 5.8 and did not exhibit, to the same extent, the downward diffusion of applied cobalt.

It was seen, from the results of the bulk soil sampling, that where increases in extractable cobalt did result from cobalt application, the increases were larger from the cobalt sulphate application than the equivalent EDTA application. This is reflected for all of the sites in the infiltration study where it is evident that there was less cobalt present in the top 6 cm of soil as a result of Co EDTA application as with $CoSO_4$ application.

It was previously suggested that a large proportion of the EDTA complex was absorbed by the herbage at the time of application, since an organo-metal complex would be more easily absorbed through the leaf cuticle than the metal salt. Less cobalt would thus enter into the soil from the EDTA than the sulphate application.

9.2.6 PLANT-AVAILABILITY OF EXTRACTABLE SOIL COBALT

It is evident, from the results of the herbage and soil sampling, as presented in Figures 9.1 to 9.3 and 9.5 to 9.7 that the extractable soil cobalt quantities did not reflect

trends observed in the plant cobalt levels. This is especially the case with the sulphate treatments. Whereas the herbage cobalt levels diminished over a period of 20 months, in the cobalt sulphate treatments, the extractable soil cobalt did not exhibit a concomitant decrease. Indeed in most cases the acetic acid-extractable cobalt levels increased over the experimental period.

This suggests that the applied cobalt was initially available to the plant roots but, over time, became non-available because of sorption processes by the soil. This plant-unavailable fraction would, to a large extent, remain extractable by acetic acid. The increased extractability of applied cobalt with time may have resulted from an increased association with soil manganese oxides. It was suggested, in Chapter 6, that although cobalt may initially be sorbed predominantly by the iron oxides of the soil oxide fraction, with time it may become irreversibly sorbed on the manganese oxides because of a greater sorption energy between cobalt and manganese oxide.

The results of Chapter 3, on the extractability of native soil cobalt, showed that acetic acid dissolved a much larger proportion of the soil manganese than soil iron. Therefore, because of a greater association between supplementary cobalt and the soil manganese oxides, with time, acetic acid would extract more cobalt.

Figure 9.12 shows the relationship between the cobalt concentration in the pasture herbage and the extractable cobalt in the soil for the control areas and sulphate plots at the sampling times of October 1979 and June 1981. It is evident that the herbage cobalt concentration bore little relationship to the acetic acid-extractable soil cobalt, for both native and applied cobalt. The results of the pot trials, in Chapters 7 and 8, also indicated that acetic acid was inadequate in prediciting the levels of plant-available cobalt in soil.

However, when the herbage cobalt concentration is compared with the acetic acid-extractable cobalt concentrations in the top 2 cm of soil a more positive relationship is obtained. A comparison is made, in Table 9.4, between the correlations made by the plant cobalt concentrations, over the whole sampling period, with acetic acid-extractable soil cobalt obtained either by soil sampling to 20 cm or 2 cm in both the control areas and sulphate plots in October 1980.

Table 9.4. Correlation coefficients between herbage cobalt concentration and extractable soil cobalt.

		Herbage cobalt concentration in control areas and sulphate plots			
		June 1979	Oct. 1979	June 1980	June 1981
Acetic acid Co in soil	Depth 20 cm	0.35(14)	-0.12(13)	-0.09(13)	0.73(6)
	Depth 2 cm	0.59(13)	0.37(12)	0.35(12)	0.44(5)

The number of sites sampled are given in brackets.

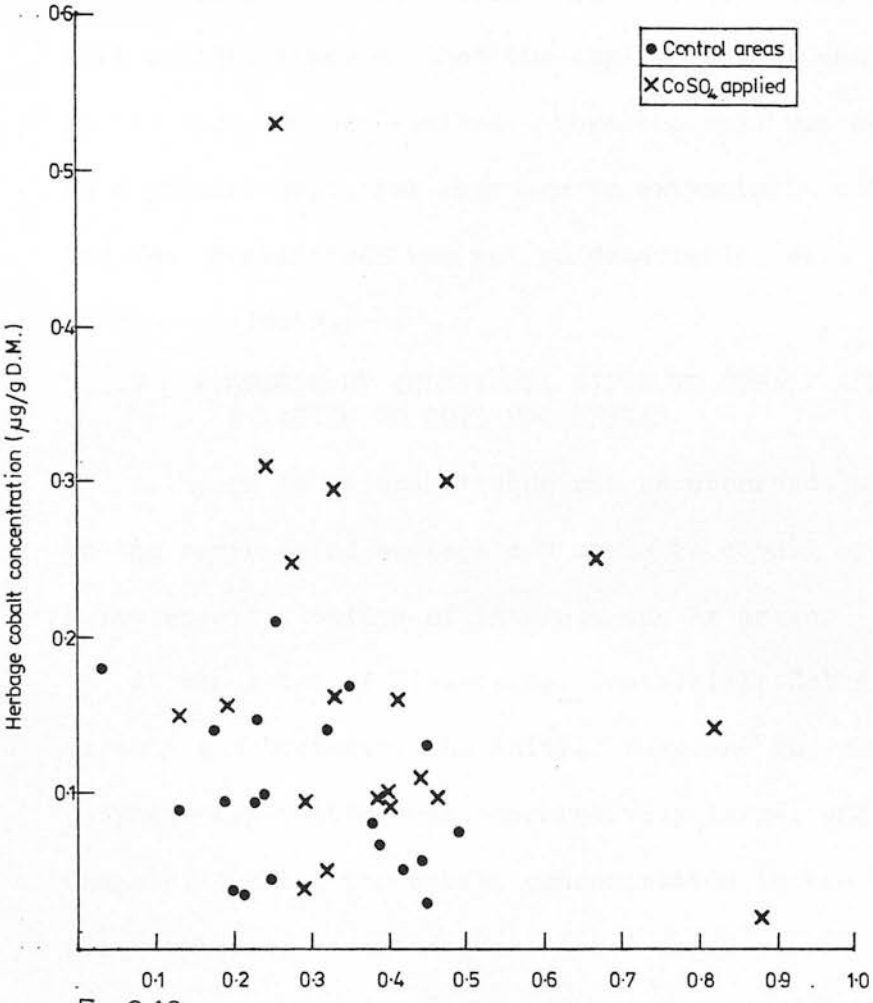


FIG. 9.12

Relationship between the cobalt content of mixed herbage and the concentration of soil cobalt extractable by 0·5M acetic acid at field trial sites.
Fourteen sites sampled in October 1979.
Six sites sampled in June 1981.

It is evident, from Table 9.4, that by sampling soil at the surface few centimetres a greater indication of the amount of plant available cobalt present was obtained. This is particularly true for soils which have been top-dressed with cobalt, since most of the applied cobalt was immobilised in the top few centimetres. When the soil was sampled to a greater depth the increase in extractable cobalt in the top few centimetres was not so detectable, as a result of dilution effects.

9.2.7 RESPONSE OF INDIVIDUAL SITES TO COBALT APPLICATION IN RELATION TO SOIL PROPERTIES

Although no general trends can be observed, with regard to the response of herbage and soils to cobalt application, a few specific points of interest can be drawn.

At the sites of Birkenside, Chapelhill, Colmsliehill, Corsbie and Huntshaw, the initial response to cobalt sulphate application was comparatively large, and at the Chapelhill site, the cobalt concentration in the herbage was maintained at an adequate level for 3 years. It is significant, however, that over this period only about 0.4 per cent of the added cobalt was taken up by the pasture herbage at this site. At other sites the uptake was less.

Sufficient herbage cobalt levels were maintained for 2 years with sulphate top-dressing at the Birkenside and Huntshaw sites. The latter site had a soil pH of 7.5, but the uptake of cobalt was comparatively large. The results

of the pot experiment in Chapter 8 indicated that soil with a pH above 7.0 would immobilise cobalt added to it, rendering it non-plant available. Sorption experiments on soils (Chapter 6) indicated that, at a soil pH of 6.9 and above, cobalt added to soil was almost totally sorbed on the solid phase. It is probable that, because of the different methods of cobalt application used in the laboratory and field experiments, different factors may have been important in determining the proportion of cobalt sorbed by the soils. In the case of the Huntshaw site, although the top soil had a pH of 7.5, the pH at the surface few centimetres, where most of the added cobalt was held, is likely to have been lower as a result of the higher organic matter concentration.

It was previously shown that the plant uptake of cobalt, in the field, was directly related to the extractable cobalt content of the top few centimetres of soil. At the sites of Chapelhill, Colmsliehill and Huntshaw, the increases in the extractable soil cobalt levels in the top 4 cm, following cobalt sulphate application, were larger than for most other soils. This was reflected in the plant uptake.

At the sites of Gateshaw, Over Whitton and Upper Chatto there was movement of applied cobalt to a depth below 6 cm and it was proposed previously that this was a result of low soil pH. The plant uptake of cobalt at these sites was comparatively poor. It is likely that cobalt sorbed by plant roots at a depth below 6 cm would be less easily translocated to the foliage than that sorbed at 2 cm depth.

The Gateshaw and Fans sites exhibited exceptionally small increases in extractable soil cobalt concentration in the top 4 cm following cobalt sulphate top-dressing. This was reflected in the low plant uptake of supplementary cobalt at both of these sites.

At the Scraesburgh site there appears to have been a lag period before the herbage cobalt concentration responded to cobalt application. The response then diminished rapidly between October 1979 and June 1981. This may have been caused by the irreversible sorption of applied cobalt as a consequence of the high manganese oxide concentration in the soil.

The herbage at Swinnie exhibited large fluctuations in the uptake of cobalt applied as cobalt sulphate solution. The uptake was not high and, only 18 months after application, the level of cobalt in the herbage became deficient again. The concentration of extractable cobalt with depth showed only a small increase in the extractable level in the top few centimetres. There also appears to have been a movement of the added cobalt to below 6 cm depth. The clay and the iron and manganese oxide contents of this soil were extremely low and this, along with the low pH (5.4) would preclude sorption of cobalt by the solid phase to a large extent.

The herbage cobalt levels at Whitfield showed a low response to cobalt top-dressing and this was probably attributable to the extremely high soil manganese content of 998 µg/g (as measured by nitric-perchloric acid soil digest). This result is in agreement with the findings

of Adams et al. (1969), who showed that plants grown on soils containing over 1,000 µg/g total manganese were unlikely to benefit from the soil application of a cobalt fertiliser. Poole et al. (1974) reported very low plant uptake of cobalt from soils with normal cobalt levels, but with manganese levels of 1,000 µg/g or above.

9.3 Conclusions

Some of the variation observed in the herbage cobalt concentration between samplings may be attributable to differences in maturity of the pasture sward at the times of sampling; there being dilution effects in the spring because of the high rate of carbohydrate accumulation compared with the uptake of soil nutrients.

The species composition of the sward will also influence the concentration of cobalt in the herbage and, from the foregoing results, it is evident that a higher proportion of clover in the sward will increase the concentration of cobalt in the herbage. However, herbage factors are likely to have caused only a small proportion of the large variation observed between sites in the uptake of fertiliser cobalt.

The fact that soil series appeared to have only a small influence on the uptake of applied cobalt, indicates that more local soil factors were of importance. One condition which was not monitored was the drainage status of the sites. Although the soil series classification takes into consideration the drainage status of the soil it was found, in some cases, that there was severe waterlogging on soils classified as being freely drained. The large effect of soil waterlogging on soil cobalt extractability by acetic acid has already been observed (Chapter 5) and it is probable that the cobalt uptake by pasture herbage over a growing season

would be influenced by the soil moisture status. However, it was concluded, in Chapter 3, that unless there were large differences in soil moisture status, variability in potentially plant-available cobalt would be governed by the chemistry of the soil rather than variability in soil moisture.

At a soil pH of 5.9, or over, the concentration of cobalt in the herbage was indirectly related to soil pH in the control areas. This was in agreement with the results of the pot experiment, in Chapter 7, in which the uptake of native cobalt by ryegrass was negatively correlated with soil pH. However, in the field trials this relationship between herbage cobalt concentration and soil pH was not obtained at soil pH below 5.9.

Contrary to the results of the pot experiment in Chapter 8, the uptake of supplementary cobalt by herbage in the field was independent of soil pH. It was suggested previously that the differences observed in the results from the pot and field experiments may have been a consequence of the different methods of cobalt application to the soil. The concentrations of cobalt added to soil in both experiments were equivalent (0.5 ppm), but the top-dressing onto the field soils caused cobalt to become immobilised in the top few centimetres of soil. In the pot experiment the supplementary cobalt was mixed intimately with soil and the ryegrass roots in the pots were then able to absorb the supplementary cobalt down to a depth of 16 cm. There was no possibility of foliar uptake of cobalt in the pot experiment.

It is of interest, therefore, that the increase in herbage cobalt concentration was significantly greater in the field

experiment than in the pot experiment, even although the period between cobalt application and herbage sampling was longer in the field trial. The difference in cobalt uptake may have been partly caused by differences in soil pH range, plant species and moisture status in the two experiments, but the major implication of the results is that added cobalt at the soil surface is more plant-available than when incorporated to a greater depth. The latter process causes a dilution of the added cobalt and so it is held more strongly on the solid phase of the soil. The sorption experiments in Chapter 6 showed that cobalt was specifically sorbed by soil oxide material at more than one energy level. The lower the concentration of sorbed cobalt the greater was the energy with which it was bound.

The applied cobalt at the surface in the field trials will be held with less energy as a result of its relatively high concentration. It was suggested that cobalt held at the surface would be held by organic matter to a large extent. The results of the sorption experiments in Chapter 6 showed that cobalt specifically sorbed by humic and fulvic acid remained more isotopically exchangeable than on inorganic soil components. Thus the lability of cobalt held by the organic matter at the surface would be higher than at the inorganic fraction. It is also likely that the pH at the soil surface is lower than in the soil as a whole. This will also increase the lability of sorbed cobalt.

The implication for pasture cultivation in cobalt deficient areas is that there would be no advantage gained in incorporating cobalt into the seed bed before sowing pasture seed.

At most of the field trial sites, the application of cobalt sulphate at 6 kg/ha did not supply adequate cobalt to the pasture over a 3 year period, most of it becoming immobilised in the soil. A top-dressing of 2 kg/ha, as is commonly used, would be totally inadequate in alleviating cobalt deficiency in these soils. It is possible, however, that an application of cobalt sulphate every 3 years on permanent pasture would gradually increase cobalt reserves in the top few centimetres of soil. As the sites for specific sorption of cobalt, on the soil oxides and organic matter, became filled the energy of sorption would decrease so that a smaller percentage of the sorbed cobalt would be immobilised. With further additions of cobalt it could enter into competition for cation exchange sites on the clay minerals, oxides and organic matter. Cobalt in this form would be plant available. Consequently, smaller and less frequent, applications of cobalt would subsequently be required. However, any cultivation of the soil for arable cropping would incorporate the top few centimetres of soil with the soil below, resulting in the loss of much of the beneficial effects gained by cobalt application.

The results suggested that high amorphous oxide content in soils may cause immobilisation of added cobalt. It is thus true that soils with a high amorphous oxide content, particularly of manganese oxides, may require larger applications of cobalt to maintain a sufficient supply of plant-available cobalt.

The use of the EDTA complex of cobalt as a soil additive appears to be ineffective at increasing plant cobalt content over a number of years. Metal chelates are used in soil applications

to prevent the metal cation from entering into sorption reactions with the solid phase and so it remains available for absorption by the plant root. When Co EDTA enters the soil solution, other metal cations such as Fe^{2+} and Ca^{2+} will, by mass action, replace cobalt in the complex, causing the cobaltous cation to be sorbed by the soil minerals. A possible conclusion from the results could have been that the Co EDTA complex was leached down to below 8 cm depth in the soil, but for the above reasons, it is highly unlikely that the complex would stay intact to this depth.

It was proposed above (section 9.2.1) that Co EDTA had entered the foliage of the plants by direct absorption, thus immediately increasing the plant cobalt concentration. In serious cases of deficiency, Co EDTA may be effective in quickly raising the herbage cobalt content.

However, the residual effects would be small compared with those resulting from cobalt sulphate application.

The cobalt EDTA application rate recommended by the manufacturers was inadequate as a means of supplying sufficient cobalt to the pastures on the soils studied.

In Chapter 7 it was observed, from the results of a pot experiment, that the concentration of cobalt in red clover was similar to that in perennial ryegrass growing on the same soil, if the latter species was deficient in cobalt for animal nutrition. This tended to be the case in soils with a pH greater than 6.4. It was concluded that in pasture improvement schemes it may not be desirable to introduce clover species if this will necessitate the raising of the soil pH, possibly causing deficient cobalt levels

in both clover and grass species.

However, the results of the field experiment showed that in two soils, with pH greater than 6.4, the uptake of both native and applied cobalt was greater in clover than in grass species. It was suggested that the greater growth rate of plants in the glasshouse pot experiment and consequent high production of leaf dry matter would obscure any differences in the rates of absorption of soil cobalt by ryegrass or red clover root systems.

It can be concluded, therefore, that the sowing of clover may be effective, in the long term, at increasing the concentration of cobalt in the herbage of permanent pasture. However, in pasture swards where clover has only recently been sown, it will not be effective at increasing the pasture cobalt concentration. At the early stages of growth dry matter production will be relatively large compared to the absorption of cobalt from the soil. This would be the case particularly in soils with high pH. In cases where pasture seed has been sown on soils with a pH above 6.4, cobalt top-dressing may subsequently be required in order to obtain herbage containing an adequate concentration of cobalt for ovine nutrition.

The results of soil analysis using 0.5 M acetic acid solution showed that this extractant does not give a satisfactory indication of plant-available cobalt levels in the soil. In view of the fact that it extracts fractions of cobalt which are strongly bound by amorphous oxides, acetic acid-extractable cobalt is, to some extent, related to the concentration of soil cobalt which is potentially available rather than immediately available to plants.

It was observed that analysis, by acetic acid, of the top few centimetres of soil gave a more satisfactory indication as to the concentration of plant-available soil cobalt. This was a result of the applied cobalt remaining in the top 2 to 4 centimetres of soil. Consequently when soil is sampled to a depth of 20 cm, as in routine sampling, the change in cobalt concentration is less evident and the correlation with the increase in plant cobalt content is poor.

Although sampling of the soil to a shallow depth may be of value in measuring acetic acid extractable cobalt levels in soil previously top-dressed with cobalt, it is evident that acetic acid soil extraction has limitations as a suitable indication for plant-available cobalt. This is a consequence of its ability to extract native soil cobalt which is not plant-available.

CHAPTER 10.

GENERAL CONCLUSIONS

Native soil cobalt was shown, in the soils used in the pot and field experiments, to be associated predominantly with the iron and manganese oxides. The sorption experiments on soil constituents indicated that soil oxide materials bound cobalt with much greater energy than any other of the soil constituents studied. These experiments also showed that the more amorphous oxide materials had a greater ability to sorb cobalt than the more crystalline oxides. In the soils studied, the native cobalt is likely to be bound mainly by the amorphous oxide material which occurs mainly as coatings on the surfaces of clay minerals, the soil manganese and iron oxide contents being directly related to soil clay content.

Cobalt extractable by 0.5 M acetic acid and 0.0^4 M EDTA, as well as total cobalt, was related to the soil iron and manganese oxide contents. This was likely to have been a result of the ability of these reagents to dissolve some oxide material. However, the concentration of isotopically exchangeable cobalt, on the soil solid phase, was also directly correlated with the soil iron and manganese oxide content. It is evident, therefore, that the amorphous oxide component of soils largely controls the mobility of soil cobalt.

Indigenous soil cobalt appeared to be associated to a greater degree with the manganese oxides than iron oxides. Evidence for this was gained from the extractability studies using 0.5 M acetic acid and 0.0^4 M EDTA. The study of cobalt sorption by soils and

soil oxides, at solution cobalt concentrations around those likely to be found in soil solution, indicated that soil manganese oxides played a relatively greater role than the iron oxides.

The role of the clay mineral component of soils in holding cobalt is likely to be much less important than the soil oxides, particularly in the soils studied. The clay minerals present in the soils of south-east Scotland are predominantly of kaolinitic and illitic nature. Kaolinite and illite were shown to have a comparatively low capability for cobalt sorption. The soil oxide material present on the surfaces of these clay minerals, in the soil matrix, will be of greater significance in retaining cobalt.

However, montmorillonite held cobalt with greater energy than kaolinite and illite and it was shown to have the ability to 'fix' cobalt in its structure. Thus where soils have a high percentage of montmorillonite in the clay fraction the cobalt may be held by the clay mineral fraction to a significant extent. Soils with high montmorillonite clay content can occur in tropical and sub-tropical conditions.

Extractability studies on soils did not show any association between total, extractable or isotopically exchangeable cobalt and soil organic matter content. It was seen that the ability of humic and fulvic acids, derived from a basin peat, to bind cobalt was greater than that of the 3 clay minerals studied. However, there was greater reversibility of cobalt sorption onto the humic acid than with the montmorillonite or soil-derived oxides. Cobalt is unlikely to be sorbed on soil organic matter with as high an energy as on humic acid, and will probably be desorbed with even

greater ease. Thus soil organic matter is likely to account for only a very small proportion of native cobalt in mineral soils.

The sorption experiments on the soils showed that at the cobalt concentrations likely to be found in normal soils ($< 10^{-6}$ M) there is an excess of sites available for further specific cobalt sorption. Therefore in the movement of cobalt between the soil solution phase and solid phase the equilibrium lies towards the solid phase. The isotopic exchange studies showed that movement of labile cobalt from the solid phase into solution increased with decreasing soil pH. The extraction of soil cobalt by 0.05 M calcium chloride solution gave an indication of the amount of cobalt able to enter into solution and so the amount that it extracted was negatively correlated with soil pH.

It seems likely that the plant root absorbs cobalt exclusively from soil solution. The results of the pot experiments support this proposition to some extent. Thus the equilibrium reaction between solid phase cobalt and solution phase cobalt will influence the amount of cobalt absorbed by the plant root. Indeed the pot experiment results showed that the uptake of indigenous soil cobalt by ryegrass was negatively correlated with the proportion of the total quantity of isotopically exchangeable cobalt which was present on the solid phase. It was noted before that equilibrium in the movement of cobalt between the two phases was pH dependent and so it is not unexpected that the plant uptake of native soil cobalt was negatively correlated with soil pH in the pot experiments. In the field situation this relationship also held for soils with a pH greater than 5.9.

The uptake of native soil cobalt, in the soils studied, was not related to the total soil cobalt contents or to the amounts of cobalt extracted by acetic acid or EDTA solution.

In both field and pot experiments only a very small percentage of the native soil cobalt entered into the foliage. The results showed that in soils with pH at normal levels for pasture production, under 0.005 per cent of the total soil cobalt will be taken up by pasture herbage per annum.

Plant availability of soil cobalt is also likely to be affected by the soil moisture content. It was shown that the extractability of native soil cobalt by acetic acid increased in a soil under waterlogged conditions. However, this increase was short-lived and cobalt quickly became non-extractable under aerated conditions. The increase in extractability was probably a result of the solubilisation of the amorphous oxide fraction under anaerobic conditions. The increased lability of cobalt under anaerobic conditions would probably increase the concentration of plant-available cobalt, but, because the increase is transitory, only soil waterlogging during the growing season would affect cobalt concentration in the herbage.

It was shown that the stage of plant maturity affected the herbage cobalt concentration. Ryegrass at a later stage of growth had a greater concentration of cobalt than that at an earlier stage.

The field trial results showed that the uptake of native cobalt by grass species was less than by clover species, even where the amounts of cobalt in mixed herbage were deficient.

However, in the pot experiment, when ryegrass cobalt concentration was below 0.08 µg/g D.M., clover content also tended to be deficient with respect to animal nutrition. It was suggested that the differences in results between the two experiments were a consequence of the longer period of plant growth in the field experiment.

The addition of cobalt to soil caused an immediate increase in the amounts extractable by 0.5 M acetic acid, but over a number of weeks there was a decrease in extractable amounts, indicating that the added cobalt was becoming bound with higher energy in the soil. The results of the cobalt sorption experiments showed that cobalt sorbed by certain soil components became bound with higher energy over time. This was especially the case with soil-derived oxides and, to a lesser extent, montmorillonite.

The influence of soil oxides on the plant availability of cobalt added to soil was investigated by a pot experiment. The results showed that, although the increase in plant cobalt concentration was dependent on soil pH, it was also negatively correlated with the soil iron and manganese oxide contents. The extremely low response to cobalt application shown by herbage at one of the field trial sites was probably a result of the exceptionally high iron and manganese oxide concentrations in the soil.

It was shown, from a laboratory experiment, that in a continuously waterlogged soil both native and supplementary cobalt became mobilised and remained extractable by 0.5 M acetic acid.

It was previously stated that the mobilisation of native soil cobalt under waterlogged conditions was likely to have been a result of the reduction of the amorphous soil oxides under anaerobic conditions. Their solubility was increased and any associated cobalt was more easily dissolved by acetic acid solution. The magnitude of the increase in the extractability of supplementary cobalt indicated that a large proportion of the added cobalt had become associated with the iron oxides of the soil. Once aerobic conditions returned to the soil the cobalt was quickly immobilised again.

As previously stated, the results of cobalt sorption on soils and soil constituents indicated that the manganese oxide fraction was more important than the iron oxide fraction in cobalt sorption. This is in contrast to the results of the cobalt extractability experiment stated above. In the sorption experiments, soil was agitated in an excess of aqueous solution containing cobalt and the mobility of sorbed cobalt was increased. In this way equilibrium between cobalt sorbed on the iron oxide fraction and manganese oxide fraction would be quickly established. Because the sorption of cobalt is likely to be more energetically favourable with the manganese oxides than iron oxides most of the cobalt will be held on the manganese oxide fraction.

In the extractability experiment referred to above, cobalt was added to physically stable soil with a moisture content under 50 per cent. The mobility of the supplementary cobalt would therefore be less than in the sorption study. In most of the soils studied the iron oxide content was around 70 times that of the manganese oxide. The initial sorption of cobalt is therefore more likely to take place

on the iron oxide fraction. Because of the greater stability of the system and the lower solution content, the equilibrium between cobalt sorbed on the iron oxides and on the manganese oxides will be established after a longer period than in the sorption studies.

There were notable differences in the results of the pot and field experiments to measure the uptake of soil applied cobalt by plants. The increase in herbage cobalt content, in the field experiment, was greater than in the pot experiment and although there was a negative correlation between plant uptake of supplementary cobalt and soil pH in the pot experiment, no such relationship was observed in the field experiment.

These differences may have resulted, in part, from the variation in soil moisture conditions in the field trials causing some fluctuation in the plant availability of cobalt. Differences in plant species between sites in the field trials may have also caused the effect of soil pH to be masked. It was shown, for instance, that there was greater uptake of supplementary cobalt by clover species than grass species. The most important factor, however, is likely to have been the different methods of cobalt sulphate application in the two experiments.

Thus, in the pot experiment, applied cobalt was distributed into a greater volume of soil so that its effective concentration was lower. Cobalt sorption experiments on soil-derived oxides showed that the energy with which cobalt was specifically sorbed increased at lower cobalt concentration. It was also shown that there was an excess of sites available for the specific sorption of cobalt in intact soils and so supplementary cobalt would be quickly immobilised. Therefore, in the pot experiment, where cobalt

was applied at the rate of 0.5 μg per g soil, the plant availability of the cobalt was extremely low.

In the field trials cobalt was applied to the surface of the soil at a rate equivalent to 0.5 μg Co per g soil in the top 20 cm. It was shown, however, that even 2 years after top-dressing most of the supplementary cobalt remained in the top 4 cm of soil. The effective cobalt concentration to this depth of soil would therefore be 2.5 μg/g soil. For the reasons stated above, this cobalt would be held less strongly and so remain more plant-available than in the pot experiment. In addition the cobalt top-dressed onto pasture first came into contact with a layer containing a high proportion of organic matter. The results of the sorption experiments showed that although humic and fulvic acids, derived from soil organic matter, could specifically sorb cobalt, the reversibility of the reaction was high, as was the isotopic exchangeability of the sorbed cobalt. For this reason supplementary cobalt bound to soil organic matter would remain more plant available than that bound to the inorganic soil fractions.

In the pot experiment the cobalt was mixed with all the fractions of the soil and so the pH measurement of the bulk of the soil is likely to give an indication of the propensity of cobalt to enter solution and become plant-available. In contrast, measurement of bulk soil pH in the field experiment would not reflect the pH in the top few centimetres of pasture soil, which is likely to have a lower pH. Thus the pH of the whole soil is unlikely to give a good indication of the propensity of cobalt, sorbed in the top few centimetres, to enter into solution.

The difference in method of application of cobalt between the field and pot trial probably caused the difference in results of the comparisons between $CoSO_4$ application and Co EDTA application. Although no significant difference in the resulting herbage cobalt content, resulting from the different forms of applied cobalt, was observed in the pot experiment, cobalt applied as the EDTA complex in the field gave a significantly lower uptake of cobalt by herbage as compared to $CoSO_4$. It was suggested that at the point of application a higher proportion of the Co EDTA had entered into the pasture foliage than with $CoSO_4$. This would raise pasture cobalt concentration to a higher level in the very short term, but there would be a lower amount of supplementary cobalt in the soil available for subsequent plant uptake.

The cobalt sulphate application currently recommended for cobalt deficient pasture areas in south-east Scotland (6 kg/ha) was found to be effective at increasing pasture herbage cobalt levels to adequate concentration (0.1 μg/g D.M.), throughout a 3 year period, in less than half of the 15 trial sites. A number of sites showed deficiency in the amount of herbage cobalt only 12 to 18 months after $CoSO_4$ application. The acetic acid-extractable soil cobalt concentrations, however, did not decrease over the period of study. This is in contrast to the results of the laboratory experiment showing that added cobalt became non-extractable over time, even with fluctuations in soil moisture content. It was suggested that the difference in cobalt behaviour between the two experiments resulted from the increased

mobilisation of added cobalt at the surface of the soils in the field trials. This was caused by the relatively high concentration of organic matter at the soil surface.

The decrease in plant availability of added cobalt, observed in the field experiments, was possibly a result of cobalt being desorbed from the organic matter and being sorbed by the oxide fraction.

Despite the short term over which benefits are obtained, it can be concluded that top-dressing of pasture with cobalt when the sward length is short, is the most effective way of supplying cobalt to pasture. In many soils of south-east Scotland the applications may have to be increased, or made at more frequent intervals, in order to maintain herbage cobalt levels at sufficient concentrations for ruminant nutrition. It is possible that if cobalt is applied regularly to soil then the specific sorption sites, particularly those on the soil oxides, may become saturated. Thus subsequent additions of cobalt may remain more plant-available.

In order to increase the longevity of the effects of pasture top-dressing with cobalt it would seem imperative that the immobilisation of applied cobalt on the soil oxide fraction should be prevented. In this respect the cobalt EDTA complex is unlikely to be successful as the cobalt in the complex will be quickly replaced by ferrous ions in soil solution, causing the displaced cobalt to be sorbed by the soil. Also Co EDTA, as noted previously, is likely to be absorbed through the foliage of the pasture herbage.

The results of the glasshouse and field experiments showed that 0.5 M acetic acid soil cobalt extraction did not give a good indication of plant-available cobalt concentrations in the soils studied. This was probably a result of the solubilisation of significant proportions of the soil amorphous oxides which contained cobalt that was non-available to plants. For the same reason 0.04 M di-sodium EDTA was an inadequate soil cobalt extractant. However, in the pot experiment, if soil pH was taken into account, along with the amount of acetic acid-extractable cobalt, a better indication of the plant available cobalt concentration was obtained.

Although, in the pot experiment, the concentration of isotopically exchangeable cobalt did not correlate well with plant cobalt concentration, the proportion of the total quantity of isotopically exchangeable soil cobalt which was present on the solid phase was significantly negatively correlated with plant cobalt levels. However, for routine analysis of plant-available cobalt in soil, calcium chloride extraction appeared to be effective, from the results of the pot experiment.

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Appendix 1.

Table 1. Effect of temperature on the amounts of cobalt, iron, manganese and organic matter extracted from soil by 0.5 M acetic acid. (Chapter 3.)

The results are the average of 2 replicates.

TEMP (°C)	Extractable Co(µg/g)			Extractable Fe(µg/g)			Extractable Mn(µg/g)		
	SOIL 36	SOIL 39	SOIL 57	SOIL 36	SOIL 39	SOIL 57	SOIL 36	SOIL 39	SOIL 57
5	0.39	0.32	0.50	10.7	13.5	13.5	38.4	46.6	43.6
10	0.40	0.37	0.49	12.5	13.1	12.5	47.0	56.4	51.1
15	0.42	0.40	0.64	10.0	16.5	15.0	55.6	64.9	59.5
20	0.45	0.53	0.78*	14.1	16.1	20.4	60.8	68.6	76.8
25	0.64	0.58	0.77	18.5	20.9	26.1	72.9	91.5	99.2
30	0.54	0.98	1.03	21.0	29.5	29.9	86.5	103.8	112.7

* 1 replicate only

Organic matter (absorbance at 400 nm)		
SOIL 36	SOIL 39	SOIL 57
0.053	0.044	0.041
0.043	0.047	0.043
0.049	0.051	0.040
0.051	0.036	0.039
0.043	0.048	0.036
0.046	0.046	0.036

Table 2. Effect of time on the amounts of cobalt, iron and manganese extracted from soil by 0.5 M acetic acid. (Chapter 3).

The results are the average of 2 replicates.

Time (hrs)	Extractable Co(µg/g)		Extractable Fe(µg/g)		Extractable Mn(µg/g)	
	SOIL 36	SOIL 57	SOIL 36	SOIL 57	SOIL 36	SOIL 57
1	0.17	0.32	2.4	7.4	20.1	29.9
2	0.24	0.38	3.8	7.3	29.6	37.7
4	0.30	0.51	5.1	9.9	43.4	52.0
8	0.45	0.67	6.6	10.7	50.0	62.2
16	0.48	0.85	9.3	16.6	69.7	86.4
24	0.66	0.96	11.0	19.6	68.1	96.9
48	0.75	1.31	14.7	28.3	97.2	131.6

Table 3. Effect of soil-solution ratio on the amount of cobalt extracted by 0.5 M acetic acid. (Soil 36) (Chapter 3).

The results are the average of 2 replicates.

Wt. soil per 100 ml. soln.	Extractable Co(µg/g)
2.5	0.51
5.0	0.47
7.5	0.40
10.0	0.35*

* 1 replicate only

Appendix 2.

Table 1. Correlation matrix for total, extractable and isotopically exchangeable cobalt with certain soil parameters. (Chapter 4).

	1	2	3	4	5	6	7	8	9	10	11	12
1. Total cobalt												
2. Acetic acid cobalt	xx 0.58											
3. EDTA - cobalt	xxx 0.78	x 0.51										
4. $CaCl_2$ - cobalt	-0.19	0.18	0.07									
5. Iso. exch. cobalt (total)	x 0.48	x 0.53	xx 0.67	xx 0.63								
6. Iso. exch. cobalt (surface)	xxx 0.75	x 0.51	xxx 0.81	0.33	xxx 0.85							
7. $pH(H_2O)$	0.00	-0.07	-0.18	xxx -0.79	xx -0.59	-0.23						
8. % clay	xx 0.62	0.31	x 0.49	0.02	0.40	x 0.55	0.05					
9. Iron (from oxide)	xxx 0.91	xx 0.64	xxx 0.72	0.01	xx 0.57	xxx 0.72	-0.06	xx 0.66				
10. Manganese (from oxide)	xxx 0.83	0.21	xxx 0.80	-0.24	0.38	xx 0.66	0.06	xx 0.56	xxx 0.70			
11. % org. C	-0.23	-0.16	-0.22	0.40	0.11	-0.09	-0.39	0.03	-0.19	-0.33		
12. C.E.C.	0.27	0.01	0.20	0.39	0.29	0.16	x -0.49	0.32	0.32	0.14	xx 0.67	

xxx P < 0.001
xx P < 0.01
x P < 0.05

Appendix 3.

Tables 1, 2, 3. Effect of soil moisture on the amounts of cobalt extracted from soil by 0.5 M acetic acid. (Chapter 5).

The results are the mean of 3 replicates.

Table 1. Low moisture treatment.

No. days after cobalt applied	7			38			89			158			212			256		
SOIL	7	9	17	7	9	17	7	9	17	7	9	17	7	9	17	7	9	17
Extractable soil cobalt (ug/g)	1.05	0.91	0.54	0.87	0.61	0.51	0.77	0.38	0.35	0.90	0.37	0.49	0.64	0.33	0.35	0.86	0.32	0.49

Table 2. Periodical waterlogging treatment.

No. days after cobalt applied	4			14			66			108			184			236		
SOIL	7	9	17	7	9	17	7	9	17	7	9	17	7	9	17	7	9	17
Extractable soil cobalt (ug/g)	1.11	1.05	0.70	0.99	0.80	0.58	1.53	0.68	0.78	0.85	0.51	0.57	0.94	0.63	0.54	0.97	0.59	0.47

258		
7	9	17
0.93	0.59	0.54

Table 3. Constant waterlogging treatment.

No. days after cobalt applied	21			49			73			122			198			257		
SOIL	7	9	17	7	9	17	7	9	17	7	9	17	7	9	17	7	9	17
Extractable soil cobalt (ug/g)	1.19	1.40	1.51	0.76	0.99	0.53	1.11	1.54	0.52	1.19	2.33	0.37	1.61	3.07	2.69	1.29	1.89	3.22

Appendix 4.

Table 1. Effect of time on the percentage of added cobalt remaining in solution after sorption by soil constituents. (Chapter 6).

The results are the mean of 2 replicates.

Equilibration period (hrs)	% Cobalt sorbed		
	Montmorillonite	Soil concretion oxides	Humic acid
1	80.6	13.75	12.3
3	71.6	7.95	10.2
23	44.8	1.53	9.2
47	38.5	0.62	8.5
71	34.4	0.42	8.4
95	31.7	0.29	8.2

Table 2. Effect of solution calcium concentration on the percentage of added cobalt sorbed by soil constituents. (Chapter 6).

The results are the mean of 2 replicates.

Calcium concentration (M)	% Cobalt sorbed (Low initial Co concn.*)			% Cobalt sorbed (High initial Co concn.*)		
	Montmorillonite	Soil concretion oxides	Humic acid	Montmorillonite	Soil concretion oxides	Humic acid
0.0005	97.57	99.63	95.84	96.36	99.65	92.33
0.001	96.21	99.47	96.29	94.62	99.69	94.53
0.005	90.05	99.84	96.56	88.98	99.28	94.15
0.01	89.00	99.47	96.16	85.26	98.71	94.81
0.05	87.51	99.29	89.56	82.50	95.60	86.67
0.5	31.82	96.90	57.89	31.85	82.03	47.66

*Low cobalt concentrations: for montmorillonite - 0.05 ppm; oxides - 2.0 ppm; humic acid - 0.2 ppm.

*High cobalt concentrations: for montmorillonite - 0.2 ppm; oxides - 8.0 ppm; humic acid - 0.8 ppm.

Table 3. Effect of solution pH on the percentage of added cobalt sorbed by soil constituents at low initial cobalt concentration* (Chapter 6).

The results are the mean of 2 replicates.

Montmorillonite		Soil concretion oxides		Humic acid	
soln pH	% Co sorbed	soln pH	% Co sorbed	soln pH	% Co sorbed
7.3	98.19	6.9	99.73	5.9	95.90
6.2	83.12	6.4	99.66	5.7	95.84
3.9	26.28	5.9	99.60	5.4	94.84
2.6	21.01	3.3	93.32	5.1	93.60
2.2	20.57	2.4	75.61	4.6	90.55
2.0	19.51	2.2	62.79	3.9	81.08

Table 4. Effect of solution pH on the percentage of added cobalt sorbed by soil constituents at high initial cobalt concentration* (Chapter 6).

The results are the mean of 2 replicates

Montmorillonite		Soil concretion oxides		Humic acid	
soln pH	% Co sorbed	soln pH	% Co sorbed	soln pH	% Co sorbed
7.3	98.00	6.9	99.03	5.9	94.96
6.2	78.14	6.4	98.02	5.7	94.99
3.9	26.47	5.9	96.49	5.4	93.63
2.6	21.76	3.3	67.82	5.1	92.21
2.2	20.45	2.4	44.42	4.6	89.16
2.0	19.62	2.2	33.59	3.9	78.81

*Low cobalt concentrations: for montmorillonite - 0.05 ppm; oxides - 2.0 ppm; humic acid - 0.2 ppm.

*High cobalt concentrations: for montmorillonite - 0.2 ppm; oxides - 8.0 ppm; humic acid - 0.8 ppm.

Table 5. Effect of varying equilibrium solution cobalt concentration on cobalt sorption by soil constituents. (Chapter 6).

The results are the mean of two replicates.

Montmorillonite		Soil concretion oxides		Humic acid	
Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)
0.001	0.95	0.0001	9.99	0.00036	0.964
0.005	4.51	0.0011	49.89	0.00216	4.78
0.011	8.91	0.0024	99.76	0.00421	9.58
0.101	39.94	0.0066	199.34	0.00958	19.04
0.300	70.02	0.0445	495.55	0.0267	47.33
0.835	116.51	0.254	974.60	0.0532	94.68
Impure Birnessite		Fulvic acid		Pure Birnessite	
Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. soln Co concn (ppm)	Co sorbed (µg/g)
0.00055	9.95	0.00088	0.912	0.0006	19.87
0.0012	19.88	0.00175	1.824	0.0022	49.55
0.0083	49.18	0.0091	9.088	0.0059	98.82
0.0397	96.03	0.0189	18.11	0.0215	195.70
0.1324	186.76	0.0479	45.21	0.1785	464.30
2.36	264.05	0.0983	90.17	0.8035	834.40

Kaolinite		Illite	
Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. soln. Co concn (ppm)	Co sorbed (µg/g)
0.0012	0.0075	0.0048	0.57
0.0088	0.0419	0.0311	1.95
0.0172	0.0817	0.0632	3.73
0.0419	0.216	0.3307	16.98
0.0727	0.195	0.8165	18.43
0.0836	0.421	1.5066	49.39

Table 6. Effect of varying equilibrium solution cobalt concentration on cobalt sorption by geologically-derived minerals. (Chapter 6).

The results are the mean of 2 replicates

Goetite		Haematite		Manganite		Pyrolusite	
Equilib. Soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. Soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. Soln. Co concn (ppm)	Co sorbed (µg/g)	Equilib. Soln. Co concn (ppm)	Co sorbed (µg/g)
0.039	46.08	0.149	35.15	0.050	45.04	0.225	27.51
0.232	76.80	0.453	54.74	0.116	88.38	0.484	51.60
0.825	117.50	1.145	85.46	0.288	171.20	1.060	94.02
3.431	156.95	3.798	120.20	1.118	388.25	3.075	192.55

Table 7. Effect of time on the isotopic exchangeability of cobalt sorbed by soil constituents. (Chapter 6).

The results are the mean of 2 replicates.

Montmorillonite			Soil concretion oxide*			Humic acid		
Equilibration period	Co sorbed (µg/g)	% Co_{ie}	Equilibration period	Co sorbed (µg/g)	% Co_{ie}	Equilibration period	Co sorbed (µg/g)	% Co_{ie}
72 hours	9.49	42.72	7 days	758.5	35.0	72 hours	19.22	97.31
6 days	9.62	28.27	19 days	772.0	14.6	6 days	19.27	90.26
17 days	9.58	25.68	26 days	775.1	4.9	17 days	19.25	90.71
26 days	9.63	20.57	37 days	776.4	4.6	26 days	19.38	71.58
38 days	9.61	19.00	44 days	777.5	2.5	38 days	19.38	70.09
52 days	9.63	16.70	51 days	778.6	1.9	52 days	19.34	74.64

*Sorption carried out in 0.05 M $CaCl_2$ instead of 0.01 M $CaCl_2$.

Table 8. Equations for isotherms of cobalt sorption by soils.

The degree to which the sorption points fit the isotherms is indicated by the significance value P.

SOIL	SORPTION ISOTHERM EQUATION	P<
1	y = 1183x - 0.22	0.001
2*	y = 1986x - 0.19	0.02
3	y = 66.3x - 0.28	0.001
4	y = 99.1x - 0.40	0.001
5	y = 87.1x - 0.47	0.001
6	y = 495x - 0.36	0.001
7	y = 1643x - 0.07	0.001
8	y = 42.8x - 1.41	0.001
9	y = 57.2x - 0.24	0.001
10	y = 183x - 0.67	0.001
11	y = 287x - 1.21	0.001
13	y = 326x - 0.01	0.001
15	y = 207x - 0.94	0.001
16	y = 74.6x - 0.61	0.001
17	y = 192x - 0.80	0.001
18	y = 69.3x - 0.78	0.001
19	y = 86.0x - 0.43	0.001
20	y = 49.3x - 0.76	0.001

*One experimental value for cobalt sorption ommitted in order to obtain a more significant fit to a rectilinear isotherm.

Table 9. Effect of solution magnesium on cobalt sorption.

Aqueous solution:-

	Cobalt sorbed (µg/g)			
	$-MgCl_2$		$+MgCl_2$	
Sorbent	rep.1	rep.2	rep.1	rep. 2
Montmorillonite	1.958	1.958	1.506	1.660
Impure Birnessite	15.64	15.68	15.28	15.64
Humic acid	15.10	15.08	15.13	15.04

Ethanol solution:-

	Cobalt sorbed (µg/g)			
	$-MgCl_2$		$+MgCl_2$	
Sorbent	rep.1	rep.2	rep.1	rep.2
Montmorillonite	1.970	1.966	1.746	1.764

Appendix 5.

Table 1. Analysis of variance for plant cobalt concentration in ryegrass. (Chapter 7). Completely randomised design : 20 soils, 3 replicates.

Source of variation	Degrees of freedom	Sum of squares	Mean squares	Variance ratio	Significance
soils	19	2.341	0.123	20.997	xxx
error	40	0.235	0.005		
total	59	2.575			

s.e. of a mean soil value (3 reps.) ± 0.044.

Table 2. Analysis of variance for plant cobalt concentration in clover. (Chapter 7). Completely randomised design : 13 soils, 3 replicates.

Source of variation	Degrees of freedom	Sum of squares	Mean squares	Variance ratio	Significance
soils	12	0.109	0.009	2.913	x
error	26	0.081	0.003		
total	38	0.190			

s.e. of a mean soil value (3 reps.) ± 0.032.

Table 3. Analysis of variance for plant cobalt concentration in ryegrass. (Chapter 8). Completely randomised design : 12 soils, 2 cobalt treatments, 3 replicates, 5 missing values. $CoSO_4$ addition.

Source of variation	Degrees of freedom	Sum of squares	Mean squares	Variance ratio	Significance
soils	11	1.573	0.143	271.849	xxx
cobalt	1	0.446	0.446	848.325	xxx
soil-cobalt interaction	11	0.582	0.053	100.498	xxx
error	43	0.023	0.00053		
total	66	2.624			

s.e. of a treatment mean (3 reps.) $\pm$0.013

Estimated values for missing data:

SOIL 14 rep.C (control) 0.054 µg/g
SOIL 15 rep.C (+$CoSO_4$) 0.132 µg/g
SOIL 16 reps.A, B (control) 0.293 µg/g
SOIL 16 rep.B (+$CoSO_4$) 0.871 µg/g

Table 4. Analysis of variance for plant cobalt concentration in ryegrass. (Chapter 8). Completely randomised design : 5 soils, 3 cobalt treatments, replicates, 4 missing values. $CoSO_4$ and Co EDTA addition.

Source of variation	Degrees of freedom	Sum of squares	Mean squares	Variance ratio	Significance
soils	4	1.436	0.359	30.657	xxx
cobalt	2	0.745	0.373	31.840	xxx
soil-cobalt interaction	8	0.366	0.046	3.913	xx
error	26	0.304	0.012		
total	40	2.852			

s.e. of a treatment mean (3 reps.) ± 0.089.

Estimated values for missing data : SOIL 16 reps. A, B (control) 0.294 µg/g
SOIL 16 rep. B (+$CoSO_4$) 0.872 µg/g
SOIL 16 rep. C (+Co EDTA) 0.756 µg/g

Appendix 6.

Table 1. Ordnance Survey co-ordinates for field trial sites. (Chapter 9).

SITE	O.S. CO-ORDINATES
Birkenside	574 419
Chapelhill	448 122
Clerklands	518 239
Colmsliehill	513 421
Corsbie	602 451
E. Nisbet	676 261
Fans	625 406
Gateshaw	776 224
Huntshaw	572 397
Lochtowers	815 267
O. Whitton	761 192
Scraesburgh	675 181
Swinnie	635 158
U. Chatto	762 168
Whitfield	470 166

Table 2. Herbage cobalt and 0.5 M acetic acid extractable soil cobalt concentrations for cobalt top-dressing experiment. (Chapter 9).

The results are the average of the analysis of at least 2 replicate sub-samples.

SITE: Birkenside SPRAYED: Nov 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.086*	0.099	0.085		0.076
LOW RATE Co EDTA	0.159	0.084	0.087		0.078
HIGH RATE Co EDTA	0.205	0.348	0.072		0.083
$CoSO_4$	0.620	0.308	0.183		0.097

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.239		0.301	0.489
LOW RATE Co EDTA		0.213		0.318	0.274
HIGH RATE Co EDTA		0.295		0.321	0.434
$CoSO_4$		0.240		0.299	0.457

*Actual cobalt concentration not available. Concentration estimated from the average of the 3 subsequent samplings.

SITE: Chapelhill

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.094	0.168	0.035		0.067
LOW RATE Co EDTA	0.167	0.176	0.040		0.078
HIGH RATE Co EDTA	0.255	0.222	0.125		0.155
$CoSO_4$	0.451	0.295	0.207		0.162

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.347		0.319	0.390
LOW RATE Co EDTA		0.300		0.357	0.349
HIGH RATE Co EDTA		0.406		0.467	0.482
$CoSO_4$		0.331		0.378	0.408

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980)

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.428	1.532	1.991
2-4	0.427	0.596	0.880
4-6	0.357	0.473	0.363
6+	0.363	0.469	0.351

SITE: Clerklands

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.083	0.139	0.072		n.a.
LOW RATE Co EDTA	0.105	0.142	0.053		n.a.
HIGH RATE Co EDTA	0.095	0.089	0.035		n.a.
$CoSO_4$	0.284	0.090	0.102		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.320		0.622	n.a.
LOW RATE Co EDTA		0.447		0.607	n.a.
HIGH RATE Co EDTA		0.452		0.781	n.a.
$CoSO_4$		0.399		0.857	n.a.

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.768	1.246	1.489
2-4	0.677	1.038	0.928
4-6	0.703	0.776	0.753
6+	0.534	0.544	0.463

n.a. Results not available

SITE: Colmsliehill

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.124	0.095	0.099		0.128
LOW RATE Co EDTA	0.072	0.338	0.107		0.118
HIGH RATE Co EDTA	0.193	0.084	0.184		0.210
$CoSO_4$	0.681	0.113	0.180		0.247

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.188		0.519	0.449
LOW RATE Co EDTA		0.344		0.427	0.421
HIGH RATE Co EDTA		0.459		0.548	0.535
$CoSO_4$		0.439		0.696	0.668

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (May 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.514	n.a.	1.513
2-4	0.447	n.a.	0.800
4-6	0.355	n.a.	0.441
6+	0.342	n.a.	0.345

n.a. Results not available.

SITE: Corsbie

Sprayed: October 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.083	0.147	n.a.		n.a.
LOW RATE Co EDTA	0.103	0.508	n.a.		n.a.
HIGH RATE Co EDTA	n.a.	0.163	n.a.		n.a.
$CoSO_4$	0.585	0.247	n.a.		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.230		n.a.	n.a.
LOW RATE Co EDTA		0.313		n.a.	n.a.
HIGH RATE Co EDTA		0.389		n.a.	n.a.
$CoSO_4$		0.274		n.a.	n.a.

n.a. Results not available.

SITE: East Nisbet

Sprayed: November 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.045	0.058	0.068		n.a.
LOW RATE Co EDTA	0.089	0.060	0.101		n.a.
HIGH RATE Co EDTA	0.094	0.121	0.068		n.a.
$CoSO_4$	0.368	0.163	0.193		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.444		0.533	n.a.
LOW RATE Co EDTA		0.313		0.381	n.a.
HIGH RATE Co EDTA		0.296		0.513	n.a.
$CoSO_4$		0.331		0.591	n.a.

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.812	0.864	1.839
2-4	0.680	0.575	1.378
4-6	0.712	0.572	0.925
6+	0.546	0.429	0.631

n.a. Results not available

SITE: Fans

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.140	0.141	0.069		n.a.
LOW RATE Co EDTA	0.093	0.813	0.074		n.a.
HIGH RATE Co EDTA	0.072	0.145	0.109		n.a.
$CoSO_4$	0.267	0.156	0.158		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.176		0.196	n.a.
LOW RATE Co EDTA		0.128		0.180	n.a.
HIGH RATE Co EDTA		0.202		0.219	n.a.
$CoSO_4$		0.187		0.248	n.a.

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.403	n.a.	0.739
2-4	0.302	n.a.	0.452
4-6	0.272	n.a.	0.264
6+	0.235	n.a.	0.283

n.a. Results not available.

SITE: Gateshaw

Sprayed: November 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.058	0.037	n.a.		0.080
LOW RATE Co EDTA	0.136	0.044	n.a.		0.096
HIGH RATE Co EDTA	0.135	0.077	n.a.		0.155
$CoSO_4$	0.329	0.094	n.a.		0.140

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.198		0.018	0.380
LOW RATE Co EDTA		0.340		0.470	0.476
HIGH RATE Co EDTA		0.390		0.599	0.533
$CoSO_4$		0.386		0.619	0.819

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.469	0.646	0.846
2-4	0.503	0.847	0.891
4-6	0.528	0.677	0.696
6+	0.511	0.573	0.753

n.a. Results not available

SITE: Huntshaw

Sprayed: November 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.045	n.a.	0.024		n.a.
LOW RATE Co EDTA	0.061	n.a.	0.035		n.a.
HIGH RATE Co EDTA	0.120	n.a.	0.056		n.a.
$CoSO_4$	0.477	n.a.	0.130		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.345		0.333	n.a.
LOW RATE Co EDTA		0.274		0.612	n.a.
HIGH RATE Co EDTA		0.367		0.358	n.a.
$CoSO_4$		0.233		0.444	n.a.

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.534	0.786	1.576
2-4	0.467	0.808	0.751
4-6	0.434	0.478	0.556
6+	0.414	0.494	0.479

n.a. Results not available

SITE: Lochtowers

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.121	0.028	0.037		n.a.
LOW RATE Co EDTA	0.143	0.036	0.039		n.a.
HIGH RATE Co EDTA	0.159	0.034	0.044		n.a.
$CoSO_4$	0.311	0.022	0.076		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.452		0.490	0.547
LOW RATE Co EDTA		0.454		0.504	0.610
HIGH RATE Co EDTA		0.538		0.641	0.625
$CoSO_4$		0.879		0.727	0.813

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.407	0.958	2.159
2-4	0.484	0.790	1.063
4-6	0.516	0.770	0.702
6+	0.560	0.709	0.653

n.a. Results not available

SITE: Over Whitton

Sprayed: November 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.038	0.045	0.094		n.a.
LOW RATE Co EDTA	0.108	0.050	0.150		n.a.
HIGH RATE Co EDTA	0.077	0.075	0.321		n.a.
$CoSO_4$	0.135	0.100	0.103		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.249		0.352	0.488
LOW RATE Co EDTA		0.238		0.340	0.385
HIGH RATE Co EDTA		0.268		0.406	0.378
$CoSO_4$		0.397		0.539	0.698

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.596	0.686	1.539
2-4	0.469	0.653	1.189
4-6	0.372	0.495	0.797
6+	0.321	0.368	0.540

n.a. Results not available

SITE: Scraesburgh

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.077	0.094	0.400		0.049
LOW RATE Co EDTA	0.086	0.171	0.123		0.039
HIGH RATE Co EDTA	0.125	0.162	0.085		0.051
$CoSO_4$	0.109	0.531	0.186		0.049

Treatment	Extractable cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.232		0.241	0.422
LOW RATE Co EDTA		0.322		0.402	0.406
HIGH RATE Co EDTA		0.280		0.319	0.371
$CoSO_4$		0.254		0.406	0.321

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980)

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.863	1.148	1.809
2-4	0.676	0.833	1.425
4-6	0.449	0.637	0.601
6+	0.382	0.503	0.488

SITE: Swinnie

Sprayed: November 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.060	0.088	0.069		n.a.
LOW RATE Co EDTA	0.156	0.329	0.096		n.a.
HIGH RATE Co EDTA	0.180	0.139	0.124		n.a.
$CoSO_4$	0.303	0.038	0.143		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.133		0.238	0.218
LOW RATE Co EDTA		0.174		0.221	0.286
HIGH RATE Co EDTA		0.245		0.293	0.354
$CoSO_4$		0.293		0.415	0.451

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.194	0.495	0.744
2-4	0.180	0.439	0.847
4-6	0.182	0.379	0.498
6+	0.164	0.288	0.344

n.a. Results not available

SITE: Upper Chatto

Sprayed: November 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.054	0.034	0.122		n.a.
LOW RATE Co EDTA	0.143	0.041	0.273		n.a.
HIGH RATE Co EDTA	0.072	0.059	0.327		n.a.
$CoSO_4$	0.192	0.094	0.119		n.a.

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.214		0.324	0.454
LOW RATE Co EDTA		0.202		0.357	0.318
HIGH RATE Co EDTA		0.276		0.454	0.486
$CoSO_4$		0.291		0.527	0.565

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.442	0.702	1.427
2-4	0.463	0.534	0.947
4-6	0.470	0.502	0.712
6+	0.382	0.459	0.608

n.a. Results not available

SITE: Whitfield

Sprayed: May 1978

Treatment	Herbage cobalt (µg/g D.M.)				
	June 1979	October 1979	June 1980		June 1981
CONTROL	0.036	0.179	0.025		0.032
LOW RATE Co EDTA	0.041	0.129	0.028		0.039
HIGH RATE Co EDTA	0.043	0.107	0.049		0.114
$CoSO_4$	0.084	0.152	0.051		0.127

Treatment	Extractable soil cobalt (µg/g)				
		October 1979		October 1980	June 1981
CONTROL		0.210		0.264	0.255
LOW RATE Co EDTA		0.270		0.403	0.323
HIGH RATE Co EDTA		0.326		0.422	0.366
$CoSO_4$		0.303		0.489	0.475

Extractable soil cobalt (µg/g) at 2 cm intervals of depth from surface (October 1980).

Depth interval (cm)	Treatment		
	CONTROL	HIGH RATE Co EDTA	$CoSO_4$
0-2	0.400	1.133	1.586
2-4	0.356	1.079	1.322
4-6	0.302	0.669	0.748
6+	0.380	0.606	0.608

Soil Series	Geological Origin	Soil Description
Belses	Silurian shales and greywackes. Upper Old Red Sandstone Sediments.	Brown forest soil with gleyed B and C horizons. Fine textured. Imperfectly drained.
Cessford	Sandstones of Upper Old Red Sandstone Series. Shales and marls interbedded with the sandstones contribute to the clay and silt grades.	Non-calcareous gley of loam texture. Poorly drained.
Darvel	Fluvioglacial sands and gravels.	Brown forest soil with sandy loam texture. Freely drained.
Eckford	Glacial lake deposits and fluvioglacial sands. Sands derived mainly from sandstones of Upper Old Red Sandstone Formation.	Brown forest soil of low base status. Coarse textured. Freely drained.
Ettrick	Grey and reddish-brown greywackes, flagstones and shales.	Non-calcareous gley soil. Drainage class poor due to the fine texture of parent till.
Hobkirk	See Cessford series.	Brown forest soil of low base status. Sandy loam texture. Freely drained.
Kedslie	See Ettrick series.	Brown forest soil with gleyed B and C horizons. Fine textured. Imperfectly drained.

Soil Series	Geological Origin	Soil Description
Lauder	Upper Old Red Sandstone conglomerates and sandstones.	Developed on shallow stony loam till over solid conglomerate. Brown forest soil of low base status. Freely drained.
Sourhope	Andesitic lavas, mostly of acidic nature.	Developed on reddish-brown rubble of loam texture. Brown forest soil of low base status. Freely drained.
Winton	Carboniferous sediments with some lavas.	Brown forest soil with gleyed B and C horizons. Sandy clay loam. Imperfectly drained.